Exercises

Introduction

Certain, more general Exercises presented here can be solved using Excel and Maple or Mathematica. These programs must be provided by the users but they are quite popular nowadays.

Modeling exercises might be carried out using ZView, LEVM, or other commercial programs supplied by the hardware manufacturers. Zview is one of the most popular and versatile programs and it has been chosen here to carry out simulations and approximations. It is a commercial program and must be purchased separately from Scribner Ass., http://www.scribner.com/. However, Exercises from this book can be solved using the commercial version of ZView because the data files *.z presented here were specially prepared by Derek Johnson from Scribner Associates Inc.[1]

The same task might be carried out using J.R Macdonald's LEVM program[1] which is available on-line for free. It allows also creation of any new circuit which is not in the library using simple FORTRAN programming. It provides also some tools for data preparation and display. However, at the beginning, one must learn how to prepare the input data and how to use many control parameters.

Another program, Multiple EIS Parameterization, based on the LEVM was developed by Kumho Petrochemical Ltd. It is called MEISP and might be downloaded for free from: http://impedance0.tripod.com/MEISP3trial.zip from E. Barsoukov's Web page.[2]

There are several other commercial programs supplied with the equipment which can also be used.

Another free program used here is KKtest written by B. Boukamp and available free on the Internet.[3] It is also presented in the Exercises.

ZView

Although it is possible to simulate simpler circuits using Excel there are tools which can make this process easier. ZView program allows for manual construction of the electrical equivalent circuits from the predefined elements and either simulation of the complex plane and Bode plots or fitting of the experimental impedances to a model. After opening the program the screen in Fig. 2.1 appears.

Let us start with creating a simple *R*(*C*(*RC*)) circuit in displayed in Fig. 2.22 p. 30. First, press Equivalent Circuits icon  (third in the second row). A new inset appears, Fig. 2.2. By clicking right mouse button it is possible to add new elements in series or in parallel to an existing element (starting from the initial conducting line), Fig. 2.2, the following circuit, Fig. 2.3, should be constructed. Then write the values of the elements, as indicated. To continue, press Model, Fig. 2.4, Edit Fit Parameters and a new inset, Fig. 2.5, appears.

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[1] Preparation by Derek Johnson from Scribner Associates Inc of the data files for this book in a special format which can be used with the commercial version of ZView is gratefully acknowledged.

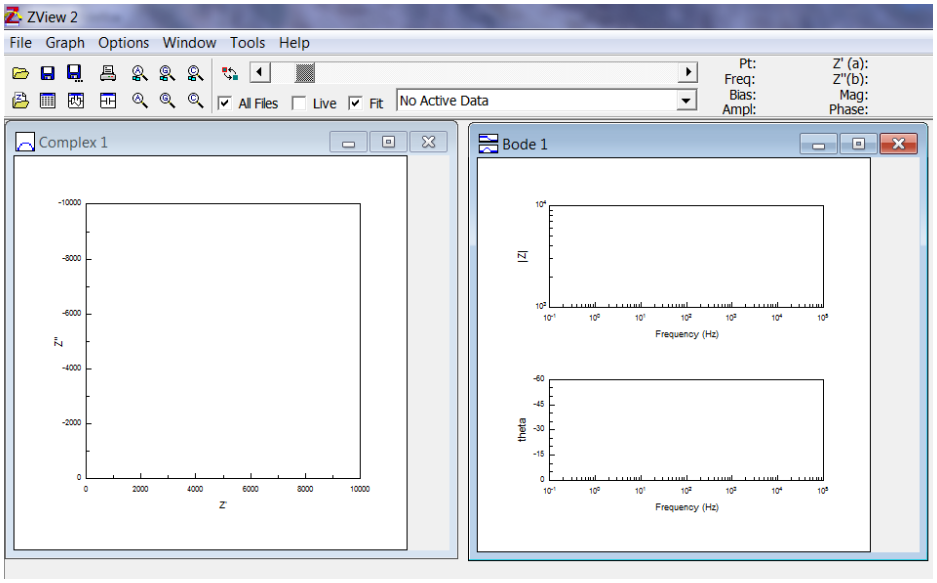


Fig. 2.1. The opening screen in ZView.

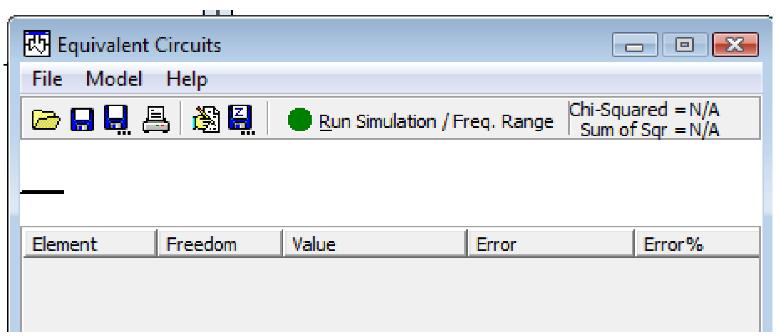


Fig. 2.2. Equivalent circuit screen.

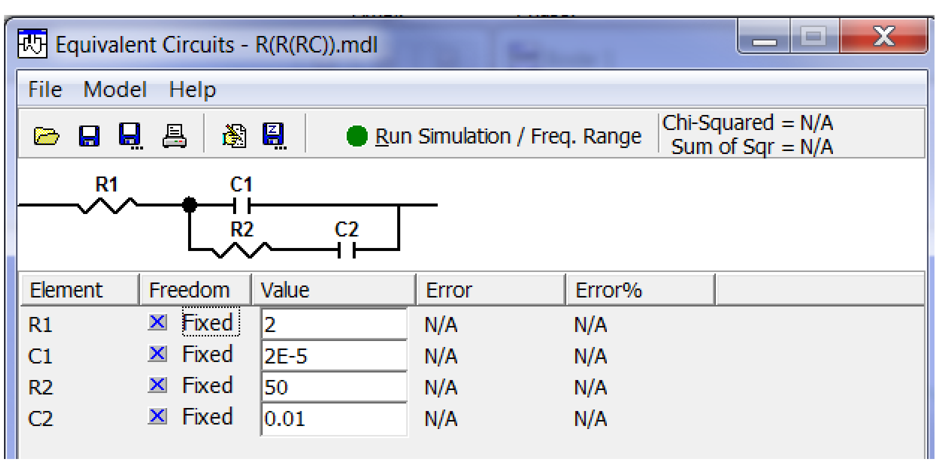


Fig. 2.3. Constructed equivalent circuit.

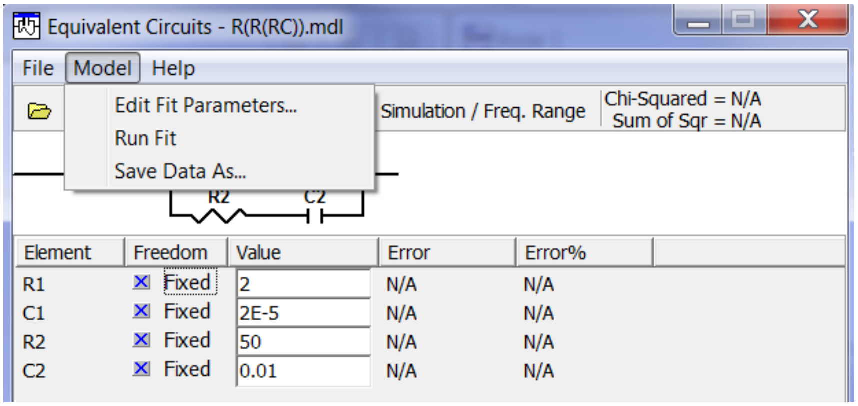


Fig. 2.4. Inserting model properties.

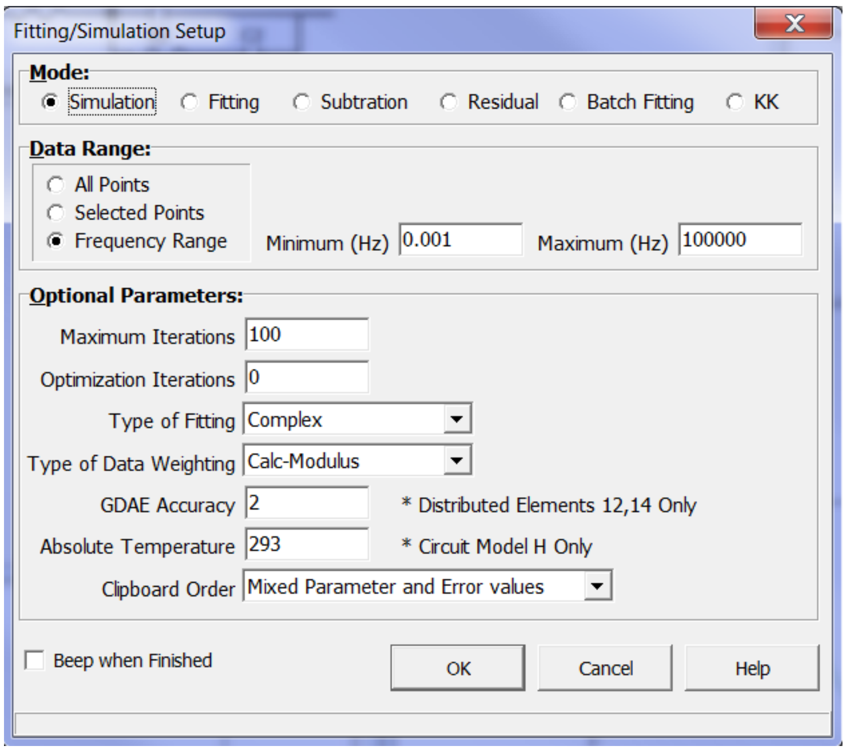


Fig. 2.5. Fitting/Simulation screen.

Set Mode to Simulations, Frequency range to 0.01 to 100000 Hz and set OK, then press Run Simulation, Fig. 2.3. The obtained complex plane and Bode plots are shown below (after zoom-in complex plane plot).

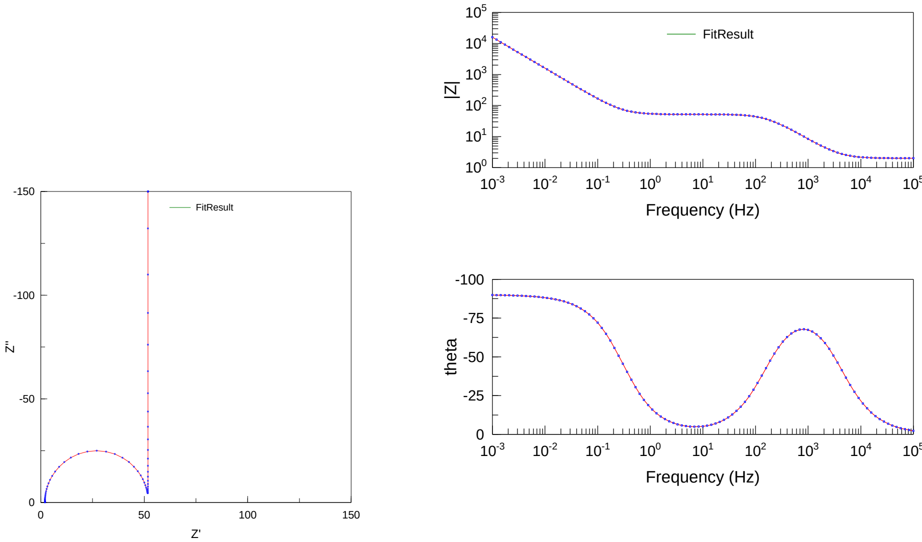
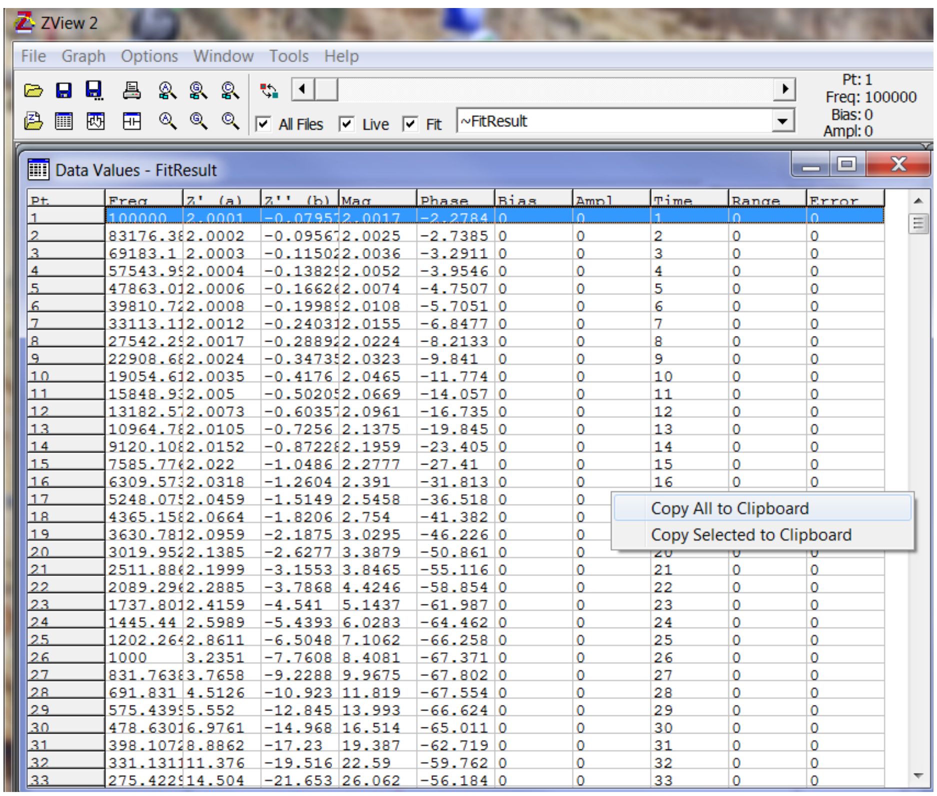


Fig. 2.6. Complex plane and Bode plots as a result of simulation of the circuit in Fig. 2.3.



Pt	Freq	Z' (a)	Z'' (b)	Mag	Phase	Bias	Ampl	Time	Range	Error
1	100000	2.0001	-0.0795	2.0017	-2.2784	0	0	1	0	0
2	83176.38	2.0002	-0.09567	2.0025	-2.7385	0	0	2	0	0
3	69183.1	2.0003	-0.11502	2.0036	-3.2911	0	0	3	0	0
4	57543.9	2.0004	-0.1382	2.0052	-3.9546	0	0	4	0	0
5	47863.01	2.0006	-0.1662	2.0074	-4.7507	0	0	5	0	0
6	39810.72	2.0008	-0.1998	2.0108	-5.7051	0	0	6	0	0
7	33113.11	2.0012	-0.24031	2.0155	-6.8477	0	0	7	0	0
8	27542.2	2.0017	-0.28892	2.0224	-8.2133	0	0	8	0	0
9	22908.6	2.0024	-0.3473	2.0323	-9.841	0	0	9	0	0
10	19054.61	2.0035	-0.4176	2.0465	-11.774	0	0	10	0	0
11	15848.93	2.005	-0.50205	2.0669	-14.057	0	0	11	0	0
12	13182.57	2.0073	-0.60357	2.0961	-16.735	0	0	12	0	0
13	10964.78	2.0105	-0.7256	2.1375	-19.845	0	0	13	0	0
14	9120.108	2.0152	-0.87228	2.1959	-23.405	0	0	14	0	0
15	7585.776	2.022	-1.0486	2.2777	-27.41	0	0	15	0	0
16	6309.573	2.0318	-1.2604	2.391	-31.813	0	0	16	0	0
17	5248.075	2.0459	-1.5149	2.5458	-36.518	0	0			
18	4365.158	2.0664	-1.8206	2.754	-41.382	0	0			
19	3630.781	2.0959	-2.1875	3.0295	-46.226	0	0			
20	3019.952	2.1385	-2.6277	3.3879	-50.861	0	0	20		
21	2511.886	2.1999	-3.1553	3.8465	-55.116	0	0	21	0	0
22	2089.296	2.2885	-3.7868	4.4246	-58.854	0	0	22	0	0
23	1737.801	2.4159	-4.541	5.1437	-61.987	0	0	23	0	0
24	1445.44	2.5989	-5.4393	6.0283	-64.462	0	0	24	0	0
25	1202.264	2.8611	-6.5048	7.1062	-66.258	0	0	25	0	0
26	1000	3.2351	-7.7608	8.4081	-67.371	0	0	26	0	0
27	831.7638	3.7658	-9.2288	9.9675	-67.802	0	0	27	0	0
28	691.831	4.5126	-10.923	11.819	-67.554	0	0	28	0	0
29	575.4399	5.552	-12.845	13.993	-66.624	0	0	29	0	0
30	478.6301	6.9761	-14.968	16.514	-65.011	0	0	30	0	0
31	398.1072	8.8862	-17.23	19.387	-62.719	0	0	31	0	0
32	331.1311	11.376	-19.516	22.59	-59.762	0	0	32	0	0
33	275.4229	14.504	-21.653	26.062	-56.184	0	0	33	0	0

Fig. 2.7. Copying the simulated data to the Clipboard.

The numerical data might be recopied to the clipboard and later to Excel or other programs. First, one should select ~FitResult to specify which data file is necessary and then data icon and right click with mouse to copy to Clipboard, see Fig. 2.7. With this knowledge we can continue to solve Exercises.

Exercise 2.1.

Generate digitalized function $E(t) = \cos(2\pi t / T_a)$ containing 64 points from 0 to 63 for the sampling time 0.01 s and wave period T_a = 0.32 s during 0.63 s. Then use Excel to carry out FFT. What information can be obtained from it?

Fill the first column with the integer numbers from 0 to 63 (64 points). Then calculate time t_i corresponding to each point, $t_i = i\Delta t$ for i = 0 to 63, and the function: $E(t) = \cos(2\pi t_i / 0.32)$, in Excel: =COS(2*PI()*B2/0.32) and copy this for all times. This is our "unknown" function which will be analyzed by the FFT. It is plotted in Fig. 2.8. The value of T (total time) equals: $T = N\Delta t = 64 \times 0.01\,\mathrm{s} = 0.64\,\mathrm{s}$. Still we have to calculate all the possible frequencies of the function which could be found from the Fourier transform. They are calculated for u from 0 to N/2 i.e. from 0 to 32, using Eq. (2.1):

$$\nu_u = \frac{u}{N\Delta t} \quad \text{for} \quad u = 0 \ldots N/2 \tag{2.1}$$

The results are displayed in Table 2.1.

To perform the FFT in Excel one should use the program Data Analysis in Data. This program is not automatically installed and may be installed by pressing File, Options, Add-Ins and adding Analysis ToolPak. It should be added that this Data Analysis tool is already on the disk and the installation from the CD is not necessary. These steps are shown in Fig. 2.9 below. Analysis ToolPak also exists in older versions of Excel.

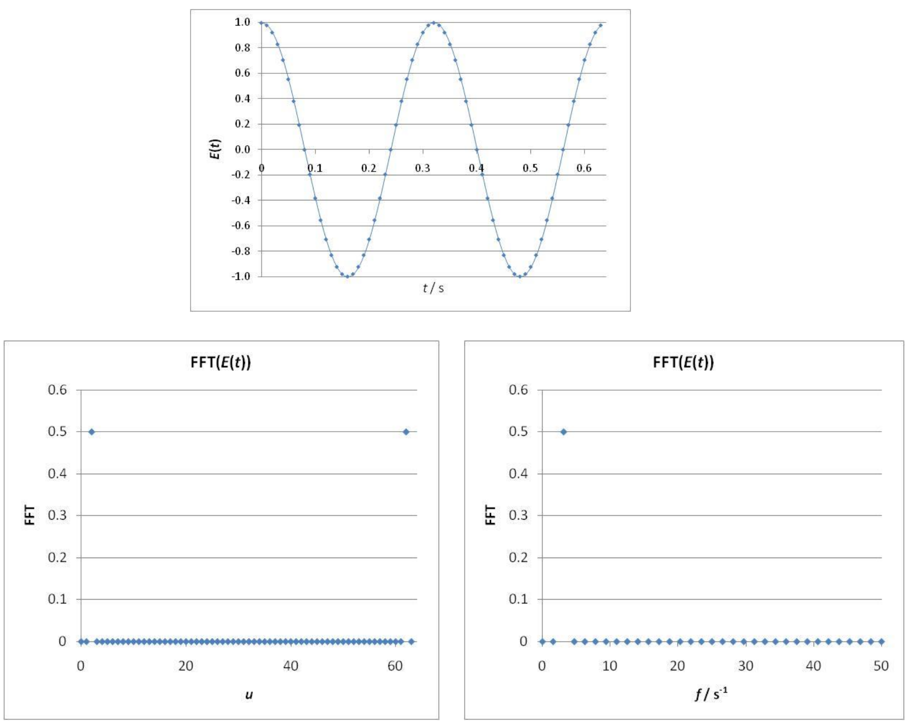


Fig. 2.8. Assumed function $E(t) = \cos(2\pi t_i / 0.32)$ (64 points) and its Fourier transform in Excel plotted versus *u* and versus frequency.

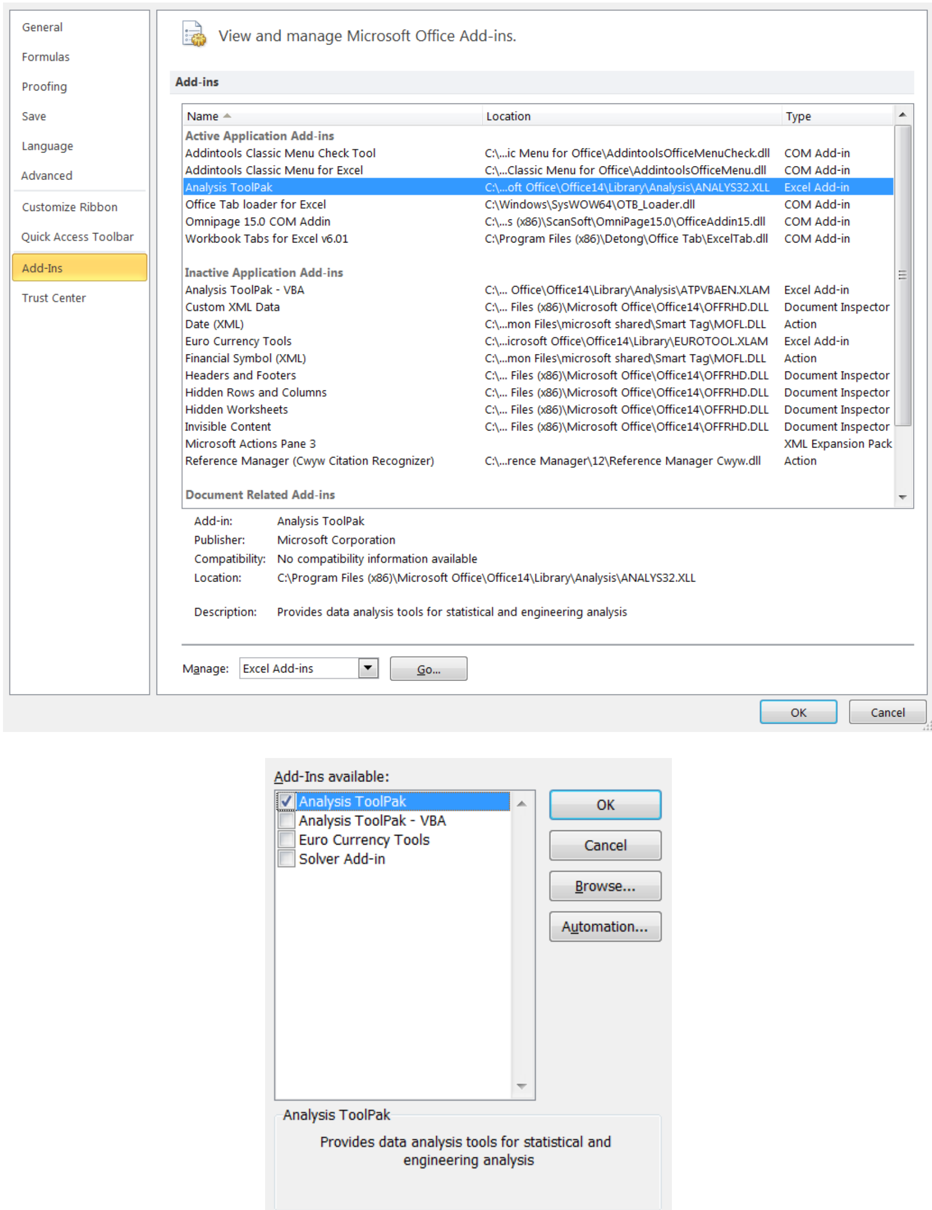


Fig. 2.9. Installation step of Analysis ToolPak.

Table 2.1. Function $\cos(2\pi t / T_a)$ and its Fourier Transform calculated in Excel.

i	t / s	$E(t)$	ν_u / s^{-1}	FFT	Re(E)
0	0.00	1.0000000	0	0	0
1	0.01	0.9807853	1.5625	0	0
2	0.02	0.9238795	**3.125**	**32**	**0.5**
3	0.03	0.8314696	4.6875	0	0
4	0.04	0.7071068	6.25	0	0
....					
28	0.28	0.7071068	43.75	0	0
29	0.29	0.8314696	45.313	0	0
30	0.30	0.9238795	46.875	0	0

31	0.31	0.9807853	48.438	0	0
32	0.32	1.0000000	50	0	0
33	0.33	0.9807853		0	0
34	0.34	0.9238795		0	0
35	0.35	0.8314696		0	0
36	0.36	0.7071068		0	0
……………					
59	0.59	0.5555702		0	0
60	0.60	0.7071068		0	0
61	0.61	0.8314696		0	0
62	0.62	0.9238795		32	0.5
63	0.63	0.9807853		0	0

In column D calculate frequencies $f_i = i / (N \Delta t) = i / (64 \times 0.01)$, that is in the first cell =A2/(64*0.01) and copy it down to $i = N / 2 = 32$. From Data, Data Analysis, choose Fourier Analysis, then as an Input Range the column containing the values of the cosine function only. The Input Range must contain one column only, do not add the time to this choice! Then specify the first cell of the output range and press OK, see Fig. 2.10.

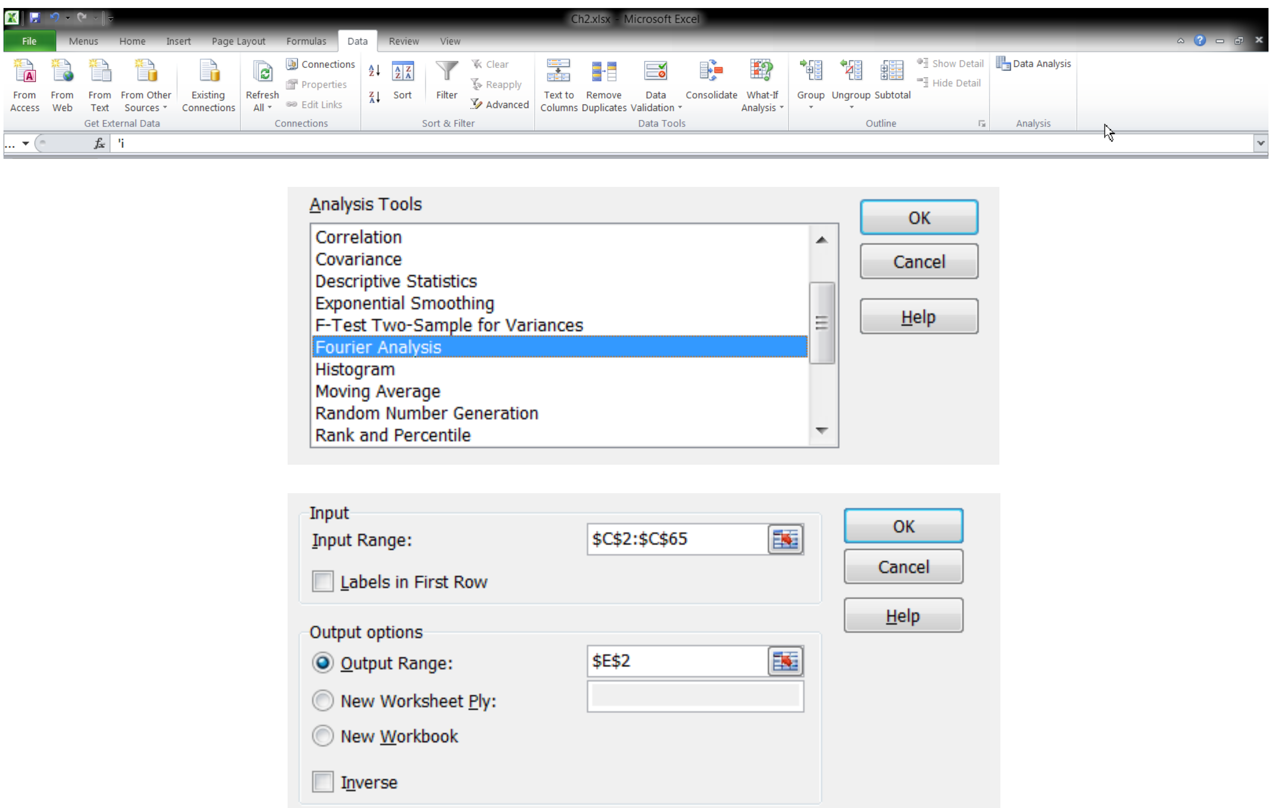


Fig. 2.10. Execution of the Fourier Analysis in Excel.

The values of the Fourier transform will appear in the column. As it is shown in Table 2.1 all the values are zeros except one value out of 32 values, for the frequency of 3.125 s^{-1}. It should be added that Excel calculates the FFT *without* dividing the sum in Eq. (2.2) by N that is by the number of points as in Eq. (2.2).

$$F(u) = \frac{1}{N} \sum_{i=0}^{N-1} f(i) \exp\left(-\frac{j2\pi ui}{N}\right) \tag{2.2}$$

This must be done manually and is displayed in column F as Re(*FFT*). Besides, Excel presents the FFT transformed data as text, not numbers. The numbers may be extracted from the text using Excel functions IMREAL() or IMAGINARY () for extracting the real and the imaginary part from the complex (text) number. In the present case all the values in the Fourier domain are already real and one can simply write: IMREAL(E2)/64 in the first cell and copy the formula to the end by double clicking in the lower right part of this cell. The results of the Fourier transform of our function $\cos(2\pi t_i / 0.32)$ are shown in Fig. 2.8 where the values of FT are plotted versus the value of *u* between 0 and 63 and versus frequency.

FT data plotted versus the value of the whole number *u* show two real values that are different from zero and equal to 0.5 for $u = 2$ and $u = 62$. All the imaginary parts of the FT are zero. As it was mentioned above the information about the frequencies is contained for *u* between 0 and $N/2 = 32$. The values of the FT versus frequency are also shown in Table 2.1; for the frequency $f = 3.125$ s^{-1} the value of the FT is 0.5. All other values are zero. This corresponds to one cosine function $\cos(2\pi f\, t) = \cos(2\pi\, 3.125 t)$, for which period is $T_a = 0.32$ s and frequency $f = 1/T_a = 3.125$ s^{-1}. This means that the function of time shown in Fig. 2.8 may be represented by the real part 0.5, the imaginary part 0 and the frequency 3.125 Hz. The phase angle is calculated according to the Eq. (2.3):

$$\varphi = \mathrm{Arg}\left(\frac{0}{0.5}\right) = 0 \tag{2.3}$$

The value of 0.5 is simply the Fourier transform of the function:

$$\frac{1}{T}\int_0^T \cos(2\pi t / T)\, e^{-j(2\pi/T)t} dt = 0.5 \tag{2.4}$$

for $T = 3.125$ s^{-1}. It should be stressed that the Fourier transform of cosine function is always real.

See the Excel file Ch2.xlsx, Worksheet Ex2.1 containing solution and figures.

Exercise 2.2.

Generate digitalized function $E(t) = \sin(2\pi t / T_a)$ containing 64 points from 0 to 63 for the sampling time 0.01 s and for wave period $T_a = 0.32$ s during 0.63 s. Then use Excel to carry out FFT. Show the plots of the function and its FT. What information can be obtained from it?

It is obvious that this function is analog of that presented in Exercise 2.1, with the same frequency but simply shifted in phase by $-\pi / 2 = -90°$:

$$\sin\left(\frac{2\pi t}{T_a}\right) = \cos\left(\frac{2\pi t}{T_a} + \varphi\right) = \cos\left(\frac{2\pi t}{T_a} - \frac{\pi}{2}\right) \tag{2.5}$$

Repeating the calculations in the same way as in

Exercise 2.1 produces the results displayed in Table 2.2.

Table 2.2. Fourier Transform of the sine function calculated in Excel.

i	*t* / s	*E*(*t*)	ν_u / s^{-1}	FFT	Re(*E*)	Im(*E*)
0	0.00	0	0	0	0	0
1	0.01	0.1951	1.5625	0	0	0
2	0.02	0.3827	**3.125**	**-32i**	**0**	**-0.5**
3	0.03	0.5556	4.6875	0	0	0
4	0.04	0.7071	6.25	0	0	0

28	0.28	-0.707	43.75	0	0	0
29	0.29	-0.556	45.313	0	0	0
30	0.30	-0.383	46.875	0	0	0
31	0.31	-0.195	48.438	0	0	0
32	0.32	-2E-16	50	0	0	0
33	0.33	0.1951		0	0	0
34	0.34	0.3827		0	0	0
35	0.35	0.5556		0	0	0
36	0.36	0.7071		0	0	0
….						
59	0.59	-0.831		0	0	0
60	0.60	-0.707		0	0	0
61	0.61	-0.556		0	0	0
62	0.62	-0.383		**32i**	**0**	**0.5**
63	0.63	-0.195		0	0	0

The assumed function and its FT are presented in Fig. 2.11. The FT of our function shows that all the real values are equal to 0, Table 2.2. FT as a function of u displays two imaginary values: -0.5j for u = 2 and 0.5j for u = 62. The frequency of the function is 3.125 s^{-1}. The phase angle is:

$$\varphi = \mathrm{Arg}\left(\frac{-0.5}{0}\right) = -\frac{\pi}{2} \tag{2.6}$$

that is -90°. FT shows three numbers characterizing our function: the real and imaginary parts and the frequency. It can also be characterized by the modulus 0.5, the phase angle $-\pi/2$ and frequency 2.125 s^{-1}.

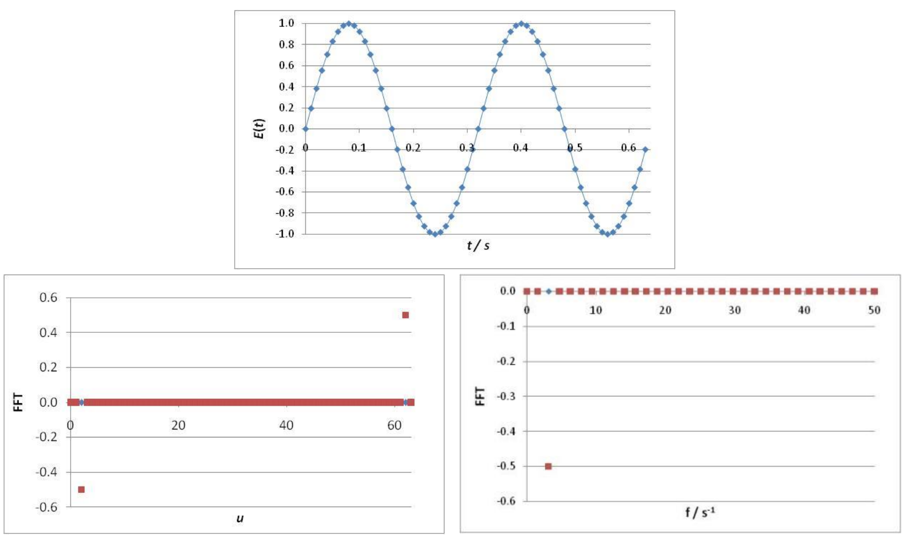


Fig. 2.11 Assumed function $\sin(2\pi t_i / 0.32)$ (64 points) and its Fourier transform (imaginary part) in Excel plotted versus *u* and versus frequency.

See the Excel file Ch2.xlsx, Worksheet Ex2.2 containing solution and figures.

Exercise 2.3.

Generate digitalized function $E(t) = \cos(2\pi t / T + \pi / 3)$ containing 64 points from 0 to 63 for the sampling time 0.01 s and for T_a = 0.32 s during 0.63 s. Then use Excel to carry out FFT. Show the plots of the function and its FT. What information can be obtained from it?

Following the procedure described above the obtained results are presented in Table 2.3 and Fig. 2.12.

Table 2.3. Fourier Transform of the sine function calculated in Excel.

i	*t* / s	*E*(*t*)	*f* / s^{-1}	FFT	Re	Im
0	0	0.5	0	0	0	0
1	0.01	0.32144	1.5625	0	0	0
2	0.02	0.13053	**3.125**	**16+27.712812921102i**	**0.25**	**0.43301**
3	0.03-	0.0654	4.6875	0	0	0
4	0.04-	0.2588	6.25	0	0	0
…						
28	0.28	0.96593	43.75	0	0	0
29	0.29	0.89687	45.3125	0	0	0
30	0.3	0.79335	46.875	0	0	0
31	0.31	0.65935	48.4375	0	0	0
32	0.32	0.5	50	0	0	0
33	0.33	0.32144		0	0	0
34	0.34	0.13053		0	0	0
35	0.35-	0.0654		0	0	0
36	0.36-	0.2588		0	0	0
…						
59	0.59	0.99786		0	0	0
60	0.6	0.96593		0	0	0
61	0.61	0.89687		0	0	0
62	0.62	0.79335		**16-27.712812921102i**	**0.25**	**-0.43301**
63	0.63	0.65935		0	0	0

In this case the FT vs. *u* presents values different from 0 for *u* = 2 and 62, they are both complex, the real parts are the same and the imaginary parts have the same value but opposite signs. The plot vs. frequency displays real and imaginary values different from zero for one frequency of $f = 3.125\ s^{-1}$, Fig. 2.12. The phase angle is:

$$\varphi = \mathrm{Arg}\left(\frac{\mathrm{Im}}{\mathrm{Re}}\right) = \mathrm{Arg}\left(\frac{0.43301}{0.25}\right) = \frac{\pi}{3} = 60° \tag{2.7}$$

From these values one can write that the original function is $\cos\left(2\pi\, 3.125t + \pi/3\right)$. The modulus of this parameter $\sqrt{0.25^2 + 0.43301^2} = 0.5$ which is the same value as in Exercise 2.1 and 2.2 as the same amplitude of the periodical function was used.

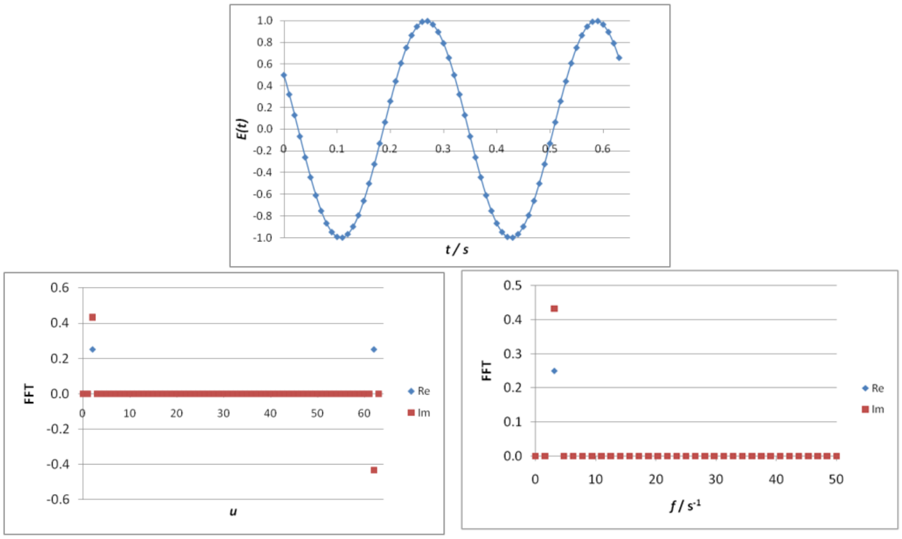


Fig. 2.12 Assumed function $E(t) = \cos(2\pi t_i / 0.32 + \pi / 3)$ **(64 points) and its Fourier transform (real and imaginary parts) in Excel plotted versus *u* and versus frequency.**

In general, cosine function always produces only the real values and sine only the imaginary values. Cosine function shifted in phase produces the real and imaginary parts from which the phase shift can be determined. In the next example we will examine FT of intrinsically aperiodic function.

See the Excel file Ch2.xlsx, Worksheet Ex2.3 containing solution and figures.

Exercise 2.4.

Generate digitalized function $E(t) = \exp(-3t_i)$ containing 32 points for the sampling time 0.01 s. Use Excel to carry out FFT. What information can be obtained from it?

The results of the FT are displayed in Table 2.4 and Fig. 2.13. It is evident that nonzero values of the FT are obtained at all frequencies; with exception of u = 0 and 16 they are all complex. The first constant value for f = 0 is simple the average value of all the experimental points. It can be noticed that for $u > N/2$ that is form u = 17 the real values are repeated in the inverse order that is: $\mathrm{Re}_{17} = \mathrm{Re}_{15}$, $\mathrm{Re}_{18} = \mathrm{Re}_{14}$, etc., while the imaginary parts change the sign: $\mathrm{Im}_{17} = -\mathrm{Im}_{15}$, $\mathrm{Im}_{18} = -\mathrm{Im}_{14}$, etc. around the central value for $u = N/2 = 16$. It must be stressed that all the frequencies are necessary to approximate the experimental points. The experimental exponential function is approximated by a sum of cosine functions with different amplitudes and different phase angles. The amplitude (modulus) at each frequency and the phase angle are displayed in Fig. 2.14. The same information is contained in the real, imaginary and frequency values as in the amplitude, phase angle and frequency. It should be stressed that FT gives exact approximation of the experimental function at each point by the sum of periodic functions. Of course, one cannot use the sum of obtained periodic functions to interpolate it between the experimental points.

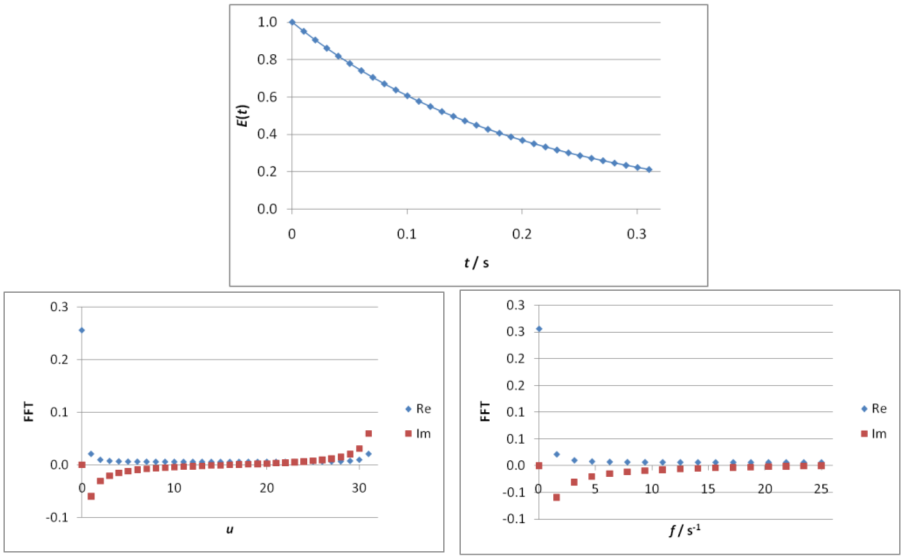


Fig. 2.13. Assumed function $E(t) = \exp(-3t_i)$ (32 points) and its Fourier transform (real and imaginary parts) in Excel plotted versus u and versus frequency.

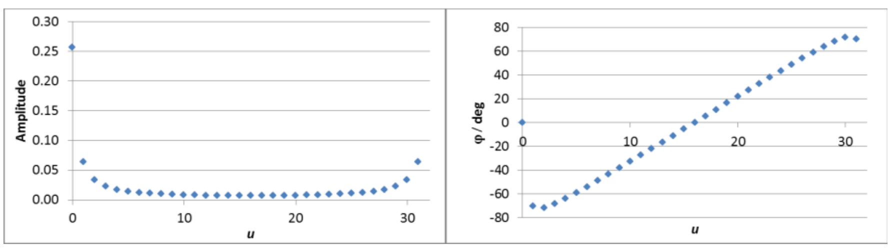


Fig. 2.14. Amplitude and the phase angle of the FT of the exponential function.

See the Excel file Ch2.xlsx, Worksheet Ex2.4 containing solution and figures.

Table 2.4. Fourier Transform of the exponential function calculated in Excel.

i	*t* / t	E(t)	f / s	FFT	Re	Im
0	0	1	0	16.3644466737332	0.2557	0
1	0.01	0.9512	1.5625	1.37442047495976-3.80411476188282i	0.0215	-0.059
2	0.02	0.9048	3.125	0.657042097331518-1.97375020281687i	0.0103	-0.031
3	0.03	0.8607	4.6875	0.516620509213295-1.30581000349564i	0.0081	-0.02
4	0.04	0.8187	6.25	0.466912846467605-0.959301198262208i	0.0073	-0.015
5	0.05	0.7788	7.8125	0.443839257694719-0.744478944461167i	0.0069	-0.012
6	0.06	0.7408	9.375	0.431321337045357-0.596016015074265i	0.0067	-0.009
7	0.07	0.7047	10.938	0.423812214347943-0.485491842302027i	0.0066	-0.008
8	0.08	0.6703	12.5	0.418987717507279-0.398553445397317i	0.0065	-0.006
9	0.09	0.6376	14.063	0.415736706772517-0.32715104664569i	0.0065	-0.005
10	0.1	0.6065	15.625	0.413475048832468-0.266396965289956i	0.0065	-0.004
11	0.11	0.5769	17.188	0.411873323035545-0.21312630311229i	0.0064	-0.003
12	0.12	0.5488	18.75	0.410736009092406-0.165171673855073i	0.0064	-0.003
13	0.13	0.522	20.313	0.409943149975871-0.120968442604471i	0.0064	-0.002
14	0.14	0.4966	21.875	0.409420341468174-7.93247761773959E-002i	0.0064	-0.001
15	0.15	0.4724	23.438	0.409122651062565-3.92783736966953E-002i	0.0064	-6E-04
16	0.16	0.4493	25	0.409025956652723	0.0064	0
17	0.17	0.4274		0.409122651062567+3.92783736966953E-002i	0.0064	0.0006
18	0.18	0.4066		0.409420341468175+7.93247761773956E-002i	0.0064	0.0012
19	0.19	0.3867		0.409943149975871+0.120968442604471i	0.0064	0.0019
20	0.2	0.3679		0.410736009092406+0.165171673855072i	0.0064	0.0026
21	0.21	0.3499		0.411873323035546+0.213126303112289i	0.0064	0.0033
22	0.22	0.3329		0.413475048832468+0.266396965289955i	0.0065	0.0042
23	0.23	0.3166		0.415736706772517+0.327151046645689i	0.0065	0.0051
24	0.24	0.3012		0.418987717507279+0.398553445397317i	0.0065	0.0062
25	0.25	0.2865		0.423812214347945+0.485491842302028i	0.0066	0.0076
26	0.26	0.2725		0.431321337045359+0.596016015074265i	0.0067	0.0093
27	0.27	0.2592		0.466912846467607+0.959301198262208i	0.0073	0.015
29	0.29	0.2346		0.516620509213299+1.30581000349564i	0.0081	0.0204
30	0.3	0.2231		0.657042097331523+1.97375020281687i	0.0103	0.0308
31	0.31	0.2122		1.37442047495977+3.80411476188283i	0.0215	0.0594

Exercise 2.5.

Generate digitalized function $E(t) = \sin(2\pi t / T_a)$ containing 256 points for the sampling time 0.2 s and T_a = 34 s. Use Excel to carry out FFT. What information can be obtained from it? Is it possible to obtain the studied function frequency from FT analysis? Repeat calculations for the same function and 2048 points. Comment on the determination of the frequency.

The simulated function and its FT are presented in Fig. 2.15 and the numerical results are in Table 2.5. The numerical calculations are shown in file Ch2.xlsx, worksheet Ex2.5. It is evident that no unique frequency is found in the Fourier space. The amplitude $|F|$ has a maximum at ν = 0.0195 s^{-1} and non-zero values are also found for higher frequencies. This problem arises from leakage; the intrinsic frequency of the assumed function is 1/34 s^{-1} = 0.02941 s^{-1} but on the list of frequencies there are only 0.019531, 0.03906, 0.05859 Hz etc. In the complete acquisition time there are 51.2/35 = 1.50588 periods of the simulated function. As there is no whole number of periods in the data acquisition time of $N\,\Delta t$ = 256×0.02 s = 51.2 s the problem of leakage appears. In such a case one should assure that whole number of periods is found in the total time. The leakage problem is also minimized (but not completely eliminated) when the total time and number of periods of the function increases. In fact, increasing number of points to 2048 i.e. the total time to 409.6 s, the frequency distribution is much more narrow and the maximum of $|F|$ is found at ν = 0.02930 Hz much closer to the experimental value of 0.02941 Hz.

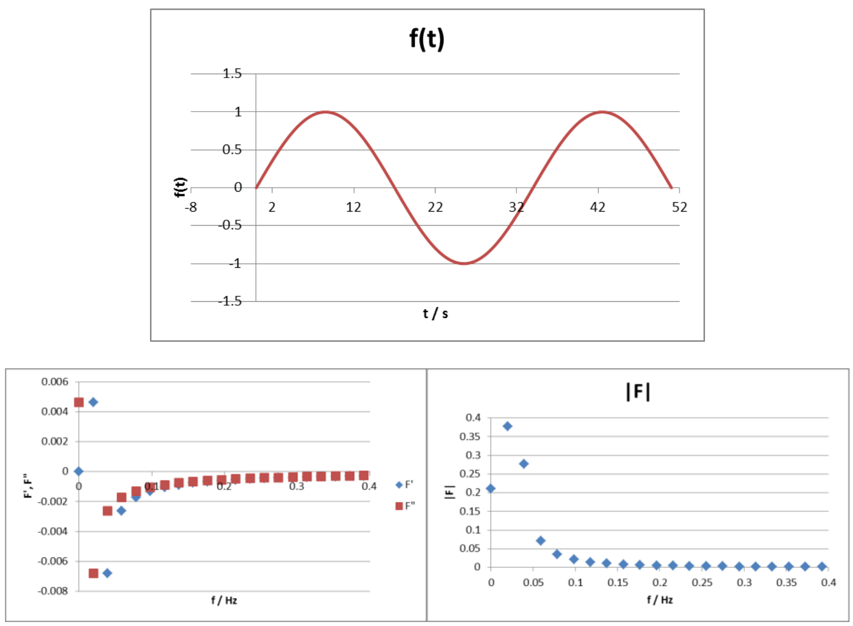


Fig. 2.15. Graph of the function $E(t) = \sin(2\pi t / 34)$ and its FT: F', F", and |F| for 256 points.

Table 2.5. Simulated function $E(t) = \sin(2\pi t / 34)$ and its FT.

i	*t*/s	sin(2*pi**t*/34)	FFT	*F*'	*F*''	|*F*|	frequency / Hz
0	0	0	54.10652052	0.211353596	0	0.211353596	0
1	0.2	0.036951499	96.7782765+1.18770775i	0.378040143	0.004639483	0.378068611	0.019607843
2	0.4	0.073852527 -	70.79939751-1.73802765i -	0.276560147	-0.006789171	0.276643466	0.039215686
3	0.6	0.110652682	-18.2085144 -0.67065930i	-0.07112701	-0.002619763	0.071175239	0.058823529
4	0.8	0.147301698	-8.92051279-0.43823669i	-0.03484575	-0.001711862	0.034887777	0.078431373
5	1	0.183749518	-5.38389990-0.33076717i	-0.02103085	-0.001292059	0.021070511	0.098039216
6	1.2	0.219946358	-3.62421433-0.2673381i	-0.01415708	-0.001044289	0.014195551	0.117647059
7	1.4	0.255842778	-2.61260783-0.22498433i	-0.01020550	-0.000878845	0.01024327	0.137254902
8	1.6	0.291389747	-1.97479646-0.19450047i	-0.00771404	-0.000759767	0.007751374	0.156862745
9	1.8	0.326538713	-1.54574152-0.1714195i	-0.00603805	-0.000669607	0.006075068	0.176470588
10	2	0.361241666	-1.24284792 -0.1532906i	-0.00485487	-0.000598792	0.004891662	0.196078431
11	2.2	0.395451207	-1.02085593-0.13864885i	-0.00398772	-0.000541597	0.004024329	0.215686275
12	2.4	0.429120609	-0.85320279-0.12656068i	-0.00333282	-0.000494378	0.003369291	0.235294118
13	2.6	0.462203884	-0.72343453-0.11640160i	-0.00282592	-0.000454694	0.002862263	0.254901961
……							
252	50.4	0.110652682	-8.92051279+0.43823669i	-0.03484575	0.001711862	0.034887777	
253	50.6	0.073852527	-18.2085144+0.67065930i	-0.07112701	0.002619763	0.071175239	
254	50.8	0.036951499	-70.7993975+1.7380276i	-0.276560147	0.006789171	0.276643466	
255	51	0	96.77827655-1.1877077i	0.378040143	-0.004639483	0.378068611	

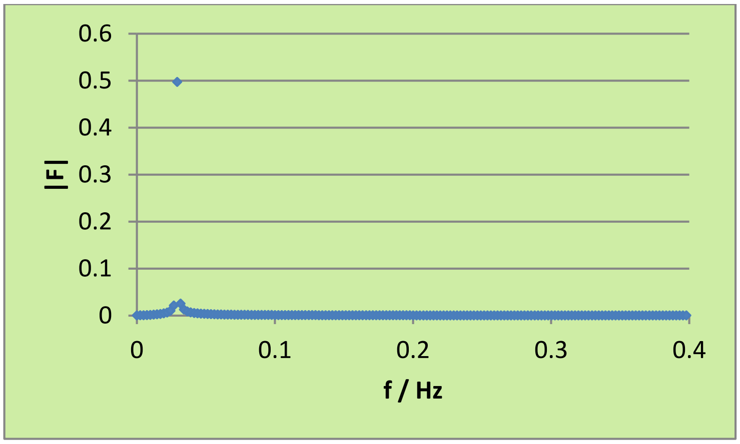


Fig. 2.16. Graph of |F| versus frequency for 2048 points.

Exercise 2.6.

Simulate curve containing sum of frequencies of functions: cos(k $2\pi t/1024$) for k = 1, 3, 7, and 13 and sin(k $2\pi t/1024$) for k = 5, 9, and 17, and t from 0 to 1023. Perform FFT, determine the frequencies and compare with the frequencies of assumed individual functions.

The frequencies of the individual functions are $k/1024$:

k	1	3	5	7	9	13	17
$10^2\nu$/Hz	0.097656	0.29296	0.48828	0.68359	0.87890	1.269531	1.66016

The FT of the total function gives the following values:

freq / Hz	Re	Im
0	0	0
0.000976563	0.5	0
0.001953125	0	0
0.002929688	0.5	0
0.00390625	0	0
0.004882813	0	-0.5
0.005859375	0	0
0.006835938	0.5	0
0.0078125	0	0
0.008789063	0	-0.5
0.009765625	0	0
0.010742188	0	0
0.01171875	0	0
0.012695313	0.5	0
0.013671875	0	0
0.014648438	0	0
0.015625	0	0
0.016601563	0	-0.5

……

and the other values of FT are null. It is obvious that all the frequencies were found correctly and the nature of the sin (imaginary) and cos (real) functions is evident. Detailed calculations are in Ch2.xlsx, Worksheet Ex2.6.

Exercise 2.7.

In order to determine the impedance of the system the applied voltage and circulating current were sampled during 0.64 s every 0.01 s. To calculate the impedance generate "experimental" data (normally they would be presented as series of numbers) using the following equations: $E(t) = E_0 \cos(\omega t)$ and $I(t) = I_0 \cos(\omega t + \pi / 3)$, where E_0 = 0.01 V, I_0 = 0.002 A, $\omega = 2\pi f = 2\pi / T_a$, T_a = 0.32 s.

In Excel generate 64 values of *i* from 0 to 63, then time every 0.01 s from 0 to 0.63 s. Next generate the values of potential and current using the following equations and copying them for all the values of time: *E* = 0.02*cos(2*PI()*B3/0.32) and *I* = 0.002*cos(2*PI()*B3/0.32+PI()/3) where cell B3 corresponds to the first value of time. In the next column the values of the frequencies are calculated using $\nu = i / (N \Delta t)$ = A3/(64*0.01) where A3 indicates the first value of the parameter *i*.

These values are displayed in Table 2.6 and file Ch2.slsx Worksheet Ex2.7. Carry out FFT of E(*t*) and *I*(*t*). FFT calculated in Excel (given in text format) should be changed into values and divided by the number of points as before using IMREAL and IMAGINARY commands. The FFT transform of *E*(*t*) is all real (column G) and the transform of current contains real (column J) and imaginary (column K) values. They are different from zero for one frequency ν = 3.125 Hz which corresponds to the assumed period $f = 1/T$ = 1/0.32 s = 3.125 Hz. The phase angle of the current is calculated using Excel function in L6: =IMARGUMENT(I5)/PI()*180 = 60° where I5 is the text result of the FFT and the angle in radians was changed into that in degrees. The same results is also be obtained in L5 using =ATAN(K5/J5)/PI()*180 = 60°, where K5 and J5 are the real and imaginary parts of the FFT (after division by *N*). The FFT of the potential and current are displayed in cells N5 and O5. Then, the impedance can be calculated as a ratio of these two values *Z* = FT(*E*)/FT(*I*); the Excel IMDIV(a,b) function may be used to divide two complex numbers. One can use numbers directly calculated by the Excel from the direct FFT (not divided by *N*) in N9 as FFT(*E*)/FFT(*I*): N9 = IMDIV(F5,I5) or in N8 from the correct values of FFT as N8 = IMDIV(N5,O5); they are of course identical. For the latter the real and imaginary parts must first be changed into the complex numbers using function N5 = COMPLEX(G5,0) for potential and O5 = COMPLEX(J5,K5) for current. Fourier transforms can also be obtained using various other programs. Of course they can be divided directly using division of complex numbers correctly. However, it is easier to use Excel functions. The phase angle of impedance is in N15 = IMARGUMENT(L8)/PI()*180, or N14 = ATAN(O11/N11)/PI()*180, and modulus of the impedance vector P12 = IMABS(N8) or P11 = SQRT(N11^2+O11^2) are calculated. It should be noticed, that then phase angle of potential is zero, that of the current is 60°, and that of the impedance -60°, as the impedance is the ratio of FFT(*E*)/FFT(*I*). The results of this example might be summarized as follows:

$\tilde{E}$ = 0.005 V, $\tilde{I}$ = $3.20\times10^{-2} + 5.54256\times10^{-2} j$ A,

$\hat{Z} = \tilde{E} / \tilde{I}$ = $2.5 - 4.33013 j$ Ω, ϕ = -60°, $|Z|$ = 5 Ω at f = 3.125 Hz.

Table 2.6. Data calculated in Excel for Exercise 2.7.

	A	B	C	D	E	F	G	H	I	J	K
1	T=	0.32s	f=	3.125	s	Ta=	0.64 s				
2	i	t	E(t)	freq		FFT(E)	Real(E)	current(I)	FFT(I)	Re(I)	Im(I)
3	0	0	0.01	0		0	0	0.001	0	0	0
4	1	0.01	0.009807853	1.5625		0	0	0.000642879	0	0	0
5	2	0.02	0.009238795	3.125	=1/0.32	0.32	0.005	0.000261052	3.20000000000001E-002+5.5425625842204E-00	0.00050	0.0008660
6	3	0.03	0.008314696	4.6875		0	0	-0.000130806	0	0	0
7	4	0.04	0.007071068	6.25		0	0	-0.000517638	0	0	0
8	5	0.05	0.005555702	7.8125		0	0	-0.000884577	0	0	0
9	6	0.06	0.003826834	9.375		0	0	-0.001217523	0	0	0
10	7	0.07	0.001950903	10.9375		0	0	-0.00150368	0	0	0
11	8	0.08	6.12574E-19	12.5		0	0	-0.001732051	0	0	0
12	9	0.09	-0.001950903	14.0625		0	0	-0.00189386	0	0	0
13	10	0.1	-0.003826834	15.625		0	0	-0.00198289	0	0	0
14	11	0.11	-0.005555702	17.1875		0	0	-0.001995718	0	0	0
15	12	0.12	-0.007071068	18.75		0	0	-0.001931852	0	0	0
16	13	0.13	-0.008314696	20.3125		0	0	-0.001793745	0	0	0
17	14	0.14	-0.009238795	21.875		0	0	-0.001586707	0	0	0
18	15	0.15	-0.009807853	23.4375		0	0	-0.001318692	0	0	0
19	16	0.16	-0.01	25		0	0	-0.001	0	0	0
20	17	0.17	-0.009807853	26.5625		0	0	-0.000642879	0	0	0
21	18	0.18	-0.009238795	28.125		0	0	-0.000261052	0	0	0
22	19	0.19	-0.008314696	29.6875		0	0	0.000130806	0	0	0
23	20	0.2	-0.007071068	31.25		0	0	0.000517638	0	0	0
24	21	0.21	-0.005555702	32.8125		0	0	0.000884577	0	0	0
25	22	0.22	-0.003826834	34.375		0	0	0.001217523	0	0	0
26	23	0.23	-0.001950903	35.9375		0	0	0.00150368	0	0	0
27	24	0.24	-1.83772E-18	37.5		0	0	0.001732051	0	0	0
28	25	0.25	0.001950903	39.0625		0	0	0.00189386	0	0	0
29	26	0.26	0.003826834	40.625		0	0	0.00198289	0	0	0
30	27	0.27	0.005555702	42.1875		0	0	0.001995718	0	0	0

	K	L	M	N	O	P
1						
2	Im(I)					
3	0					
4	0	Phi/deg		FFT(E)	FFT(I)	
5	0.0008660	60		0.005	0.000500000000000002+0.000866025403784438i	
6	0	60				
7	0			Impedance=FFT(E)/FFT(i)		
8	0			2.50000000000001-4.33012701892219i		
9	0			2.50000000000001-4.33012701892219i		
10	0		Impedance	Re	Im	|Z|
11	0			2.5	-4.330127019	5
12	0					5
13	0			Phi		
14	0			-60		
15	0			-60		
16	0					
17	0		|I|=	0.001		
18	0		|E|=	0.005		
19	0		|Z|=	5		
20	0					
21	0					
22	0					
23	0					
24	0					
25	0					
26	0					
27	0					
28	0					
29	0					
30	0					

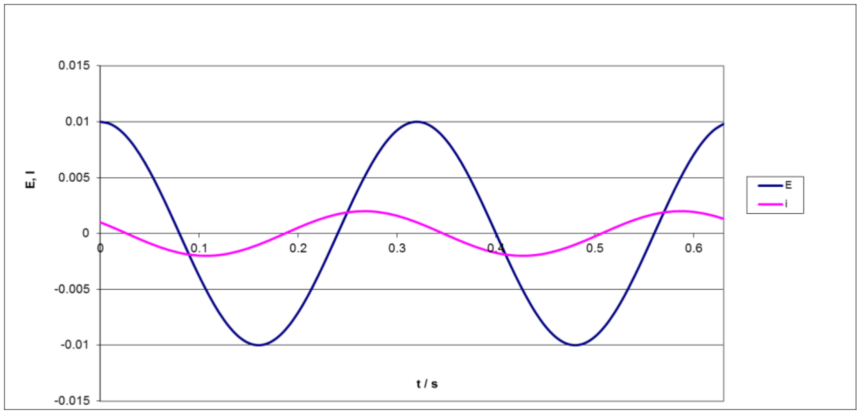


Fig. 2.17. Potential and current functions for Exercise 2.7.

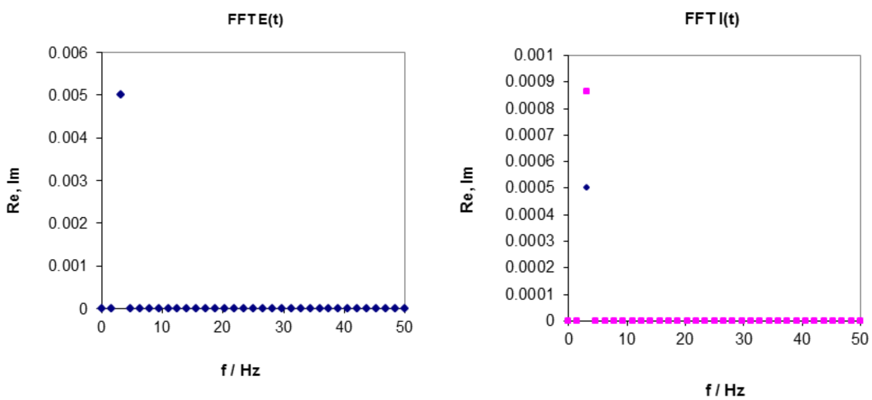


Fig. 2.18. FFT of the potential and current functions in Exercise 2.7; real part – diamonds, imaginary - squares.

Exercise 2.8.

Determine impedance using data obtained from D/A data acquisition of voltage and current. This data containing time, potential and current: t, $E(t)$, $I(t)$ in s, V, and A, respectively, can be found in file Ex2_8.txt. What is the frequency of these functions?

First, the data must be read into Excel worksheet. There are N = 512 data points sampled every 0.1 ms. The total data acquisition period is $T = N\,\Delta t = 512\times0.0001$ s = 0.0512 s. The information about the frequencies are up to $N/2$ = 256. Insert column containing i from 0 to 511 and calculate frequencies for i from 0 to 256. In the experimental data there is information about frequencies between $1/T$ = 19.53 and $1/(2\Delta t)$ = 5000 Hz. Carry out FFT of $E(t)$ (column F) and of $I(t)$ (column G). The FT values divided by N are found in columns H-J. There is only one value different form zero for ν = 625 Hz. The FT of potential and current are transferred into complex values in cells M2 and M3. The impedance is in M5 form division of two complex numbers. The results are as follows:

FFT(E) 0.00250000007908623 V

FFT(I)= 0.000161803349200174+0.000117557015932286i A

Z= 10.1127157612695-7.34731817198353i Ω

$|Z|$= 12.5 Ω, φ = -36 deg, f= 625 Hz

Exercise 2.9.

Make complex plane, Bode, and complex admittance plots of RC connection in series; R = 150 Ω, C = 40 μF.

The data might be easily prepared using Excel. For this circuit the total impedance is:

$$\hat{Z}(j\omega) = R + \frac{1}{j\omega C} = R - j\frac{1}{\omega C} \tag{2.8}$$

the modulus and then phase angle are:

$$\begin{aligned} |Z| &= \sqrt{R^2 + \frac{1}{(\omega C)^2}} \\ \varphi &= \operatorname{atan}\left(\frac{Z''}{Z'}\right) = \operatorname{atan}\left(-\frac{1}{\omega RC}\right) = -\operatorname{atan}\left(-\frac{1}{\omega RC}\right) \end{aligned} \tag{2.9}$$

and the admittance is:

$$\hat{Y}(j\omega) = \frac{1}{\hat{Z}(j\omega)} = \frac{1}{R - j\frac{1}{\omega C}} = \frac{R}{R^2 + \frac{1}{\omega^2 C^2}} + j\frac{1}{\omega C\left(R^2 + \frac{1}{\omega^2 C^2}\right)} \tag{2.10}$$

Eqs. (2.8) and (2.9) allow for the complex plane and Bode representation of impedances.

To make the graph first angular frequencies distributed 10 point per decade should be generated. Therefore, first log ω from -4 to 6 every 0.1. Then ω is calculated in column B as =10^(A3) and the formula should be recopied. Next calculate: $Z' = R = \$B\$1$; $Z'' = -1/\omega C = -1/(B3*\$D\$1)$;

$\log|Z| = \log\sqrt{Z'^2 + Z''^2} = \mathrm{LOG10(SQRT(C3\wedge 2 + D3\wedge 2))}$; $\varphi = \mathrm{ATAN}(Z''/Z') = \mathrm{=ATAN(D3/C3)/PI()*180}$;

$Y' = Z'/(Z'^2 + Z''^2) = \mathrm{C3/(C3\wedge2+D3\wedge2)}$; and

$Y'' = -Z''/(Z'^2 + Z''^2) = -\mathrm{D3/(C3\wedge2+D3\wedge2)}$, see Table 2.7 and Ch2.xlsx, Worksheet Ex2.8.

Next, the corresponding plots might be prepared using Excel or another graphing program. They are displayed in Fig. 2.19 and in the worksheet. In the complex plane plot the real part is always constant, $Z' = R$, and the imaginary part, $Z'' = -1/\omega C$, changes from zero at infinite frequency to infinity at zero frequency. The dc current cannot circulate through the circuit and the low frequency imaginary part of impedance goes to -∞ while the real part is always constant. The Bode magnitude contains two elements: R and $1/\omega C$. The plot presents a constant value $\log|Z| = \log R$ at high frequencies and a straight line with a slope -1: $\log|Z| = -\log\omega - \log C$. There is an inflection point where these two elements are identical giving the break point frequency: $\omega = 1/RC$, in our example $\omega = 166.67$ rad s^{-1}, corresponding to the time constant $\tau = RC = 6\,\text{ms}$. The Bode phase angle plot represents two bend points and changes between angle zero at high frequencies and 90° at very low frequencies. The admittance presents a semi-circle; at very low frequencies the admittance is zero (impedance infinite) and at high frequencies it is equal to 1/R as the impedance of capacitance is zero. The maximum of admittance is at $\omega = 1/RC$.

Table 2.7. Calculations of the impedance, modulus, phase angle and admittances.

IMABS =10^(A3)

	A	B	C	D	E	F	G	H
1	R=	150	C=	4.00E-05				
2	log(om)	om	Z'	Z"	log |Z|	phi	Y'	Y"
3	-4	=10^(A3)	150	-2.50E+08	8.39794	-9.00E+01	2.40E-15	4.00E-09
4	-3.9	0.000126	150	-1.99E+08	8.29794	-9.00E+01	3.80E-15	5.04E-09
5	-3.8	0.000158	150	-1.58E+08	8.19794	-9.00E+01	6.03E-15	6.34E-09
6	-3.7	0.0002	150	-1.25E+08	8.09794	-9.00E+01	9.55E-15	7.98E-09
7	-3.6	0.000251	150	-9.95E+07	7.99794	-9.00E+01	1.51E-14	1.00E-08
8	-3.5	0.000316	150	-7.91E+07	7.89794	-9.00E+01	2.40E-14	1.26E-08
9	-3.4	0.000398	150	-6.28E+07	7.79794	-9.00E+01	3.80E-14	1.59E-08
10	-3.3	0.000501	150	-4.99E+07	7.69794	-9.00E+01	6.03E-14	2.00E-08
11	-3.2	0.000631	150	-3.96E+07	7.59794	-9.00E+01	9.55E-14	2.52E-08
12	-3.1	0.000794	150	-3.15E+07	7.49794	-9.00E+01	1.51E-13	3.18E-08
13	-3	0.001	150	-2.50E+07	7.39794	-9.00E+01	2.40E-13	4.00E-08
14	-2.9	0.001259	150	-1.99E+07	7.29794	-9.00E+01	3.80E-13	5.04E-08
15	-2.8	0.001585	150	-1.58E+07	7.19794	-9.00E+01	6.03E-13	6.34E-08
16	-2.7	0.001995	150	-1.25E+07	7.09794	-9.00E+01	9.55E-13	7.98E-08
17	-2.6	0.002512	150	-9.95E+06	6.99794	-9.00E+01	1.51E-12	1.00E-07
18	-2.5	0.003162	150	-7.91E+06	6.89794	-9.00E+01	2.40E-12	1.26E-07
19	-2.4	0.003981	150	-6.28E+06	6.79794	-9.00E+01	3.80E-12	1.59E-07
20	-2.3	0.005012	150	-4.99E+06	6.69794	-9.00E+01	6.03E-12	2.00E-07
21	-2.2	0.00631	150	-3.96E+06	6.59794	-9.00E+01	9.55E-12	2.52E-07
22	-2.1	0.007943	150	-3.15E+06	6.49794	-9.00E+01	1.51E-11	3.18E-07
23	-2	0.01	150	-2.50E+06	6.39794	-9.00E+01	2.40E-11	4.00E-07

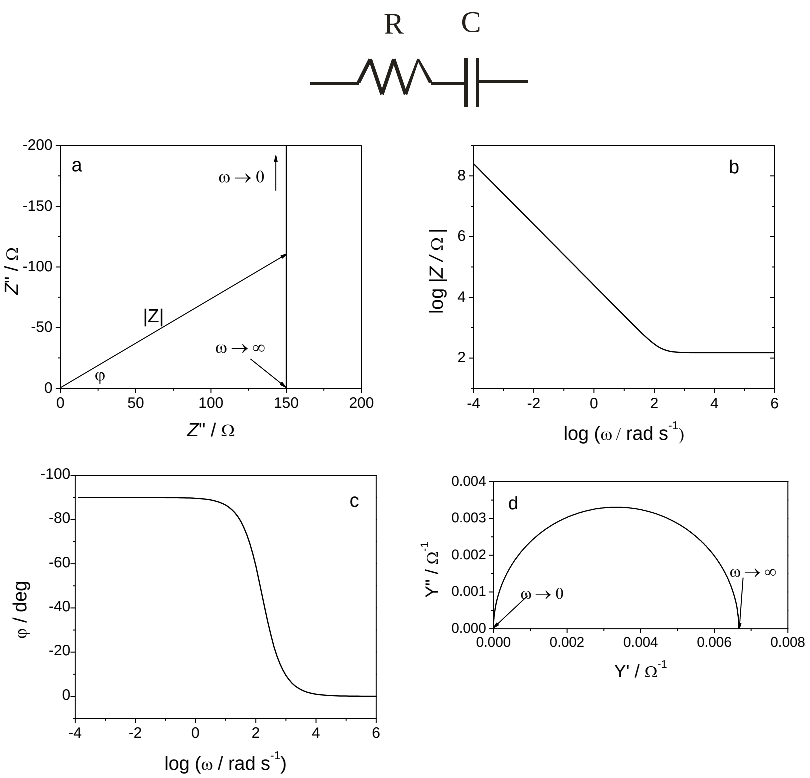


Fig. 2.19. Complex plane (a), Bode magnitude (b), Bode phase4 angle (c), and complex admittance (c) plots for R-C connection in series; $R = 150\,\Omega$, $C = 40\,\mu\mathrm{F}$.

Exercise 2.10.

Make complex plane, Bode, and complex admittance plots of (RC) connection in parallel; R = 100 Ω, C = 20 μF.

The impedance of the system is:

$$Z = \frac{1}{\frac{1}{R} + j\omega C} = \frac{R}{1 + j\omega RC} = \frac{R}{1 + (\omega RC)^2} - j\frac{\omega R^2 C}{1 + (\omega RC)^2} \tag{2.11}$$

$$|Z| = \frac{\sqrt{R^2 + \left(\omega R^2 C\right)^2}}{1 + (\omega RC)^2} \qquad \varphi = \operatorname{atan}(-\omega R\mathrm{C}) = -\operatorname{atan}(\omega R\mathrm{C}) \tag{2.12}$$

and the admittance:

$$\hat{Y} = \frac{1}{R} + j\omega C \tag{2.13}$$

Table 2.8. Calculations of the impedance, modulus, phase angle and admittances for Exercise 2.10.

	A	B	C	D	E	F	G	H
1	R=	100	C=	2.00E-05				
2	log(om)	om	Z'	Z"	log|Z|	Phi	Y'	Y"
3	-4	0.0001	1.00E+02	-2.00E-05	2.00E+00	-1.15E-05	1.00E-02	2.00E-09
4	-3.9	0.000126	1.00E+02	-2.52E-05	2.00E+00	-1.44E-05	1.00E-02	2.52E-09
5	-3.8	0.000158	1.00E+02	-3.17E-05	2.00E+00	-1.82E-05	1.00E-02	3.17E-09
6	-3.7	0.0002	1.00E+02	-3.99E-05	2.00E+00	-2.29E-05	1.00E-02	3.99E-09
7	-3.6	0.000251	1.00E+02	-5.02E-05	2.00E+00	-2.88E-05	1.00E-02	5.02E-09
8	-3.5	0.000316	1.00E+02	-6.32E-05	2.00E+00	-3.62E-05	1.00E-02	6.32E-09
9	-3.4	0.000398	1.00E+02	-7.96E-05	2.00E+00	-4.56E-05	1.00E-02	7.96E-09
10	-3.3	0.000501	1.00E+02	-1.00E-04	2.00E+00	-5.74E-05	1.00E-02	1.00E-08
11	-3.2	0.000631	1.00E+02	-1.26E-04	2.00E+00	-7.23E-05	1.00E-02	1.26E-08
12	-3.1	0.000794	1.00E+02	-1.59E-04	2.00E+00	-9.10E-05	1.00E-02	1.59E-08
13	-3	0.001	1.00E+02	-2.00E-04	2.00E+00	-1.15E-04	1.00E-02	2.00E-08
14	-2.9	0.001259	1.00E+02	-2.52E-04	2.00E+00	-1.44E-04	1.00E-02	2.52E-08
15	-2.8	0.001585	1.00E+02	-3.17E-04	2.00E+00	-1.82E-04	1.00E-02	3.17E-08
16	-2.7	0.001995	1.00E+02	-3.99E-04	2.00E+00	-2.29E-04	1.00E-02	3.99E-08
17	-2.6	0.002512	1.00E+02	-5.02E-04	2.00E+00	-2.88E-04	1.00E-02	5.02E-08
18	-2.5	0.003162	1.00E+02	-6.32E-04	2.00E+00	-3.62E-04	1.00E-02	6.32E-08
19	-2.4	0.003981	1.00E+02	-7.96E-04	2.00E+00	-4.56E-04	1.00E-02	7.96E-08
20	-2.3	0.005012	1.00E+02	-1.00E-03	2.00E+00	-5.74E-04	1.00E-02	1.00E-07
21	-2.2	0.00631	1.00E+02	-1.26E-03	2.00E+00	-7.23E-04	1.00E-02	1.26E-07
22	-2.1	0.007943	1.00E+02	-1.59E-03	2.00E+00	-9.10E-04	1.00E-02	1.59E-07
23	-2	0.01	1.00E+02	-2.00E-03	2.00E+00	-1.15E-03	1.00E-02	2.00E-07

Using calculations in Excel, the results presented in Ch2.xlsx, Worksheet Ex2.10, Table 2.8, and Fig. 2.20 are obtained. The impedance presences a semicircle; when the frequency goes to infinity, the impedance goes to zero as the impedance of the capacitor becomes zero and when the frequency goes to zero the impedance becomes real $Z = R$ as a constant dc current can flow through the circuit. The maximum of the imaginary part is observed at the frequency $\omega = 1/RC$ and RC is called the time constant of the system. As in the preceding example the imaginary part of the impedance is always negative. There are two linear parts of the Bode magnitude plot; when the frequency is very low Eq. (2.11) reduces to $|Z| = R$ and when frequency is very large the real part becomes small and $|Z| = 1/\omega C$. There is one break-point frequency on the Bode magnitude plot, when $R = 1/\omega C$ and the break-point frequency corresponds to the system time constant:

$$\omega = \frac{1}{\tau} = \frac{1}{RC} \tag{2.14}$$

In this example the time constant equals $\tau = RC = 100\,\Omega \times 20\,\mu\text{F} = 2 \times 10^{-3}$ s and the characteristic break-point frequency is 500 rad s^{-1}.

The admittance plot for RC connection in parallel is similar in shape to the impedance plot for a RC connection in series. The difference is that for the circuits containing capacitances the imaginary part of the impedance is negative and that of the admittance positive.

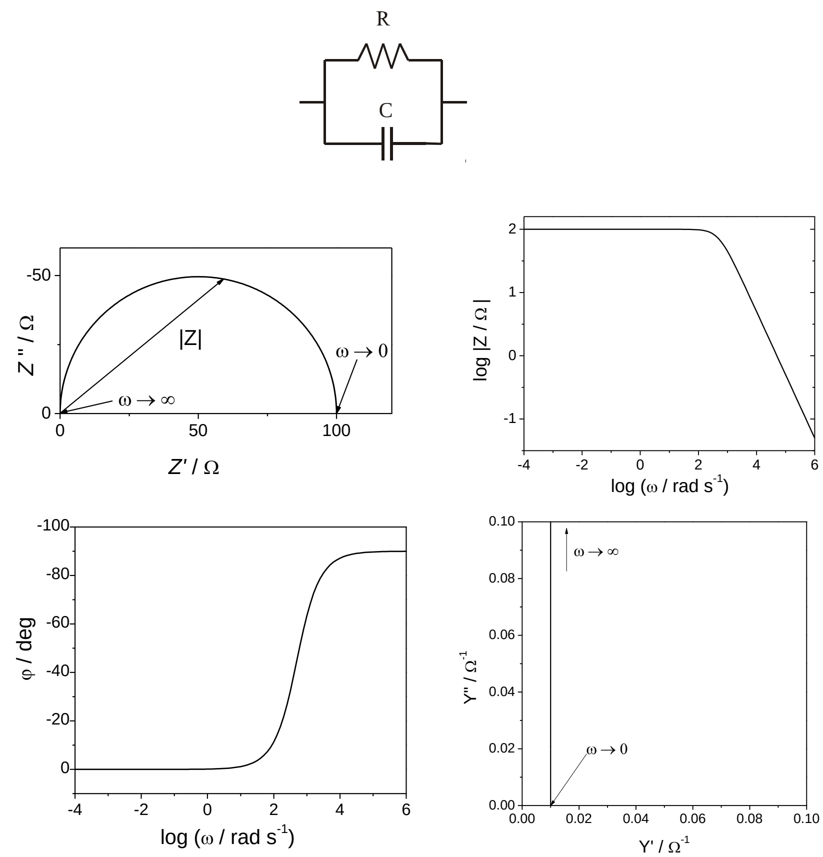


Fig. 2.20. Complex plane impedance, Bode, and complex plane admittance plots for a connection of *R* and *C* in parallel, *R* = 100 Ω, *C* = 20 μF.

Exercise 2.11.

Make complex plane, Bode, and complex admittance plots of R_s in series with the parallel connection of RC, $R_s(RC)$; $R_s = 10\ \Omega$, $R = 100\ \Omega$, $C = 20\ \mu\text{F}$.

The total impedance of the system is:

$$\hat{Z} = R_s + \frac{1}{\frac{1}{R} + j\omega C} = R_s + \frac{R}{1 + j\omega RC} = R_s + \frac{R}{1+(\omega RC)^2} - j\frac{\omega R^2 C}{1+(\omega RC)^2} \tag{2.15}$$

and the real and imaginary part of the impedance might be easily calculated. Using calculations in Excel, the results in Table 2.9 are obtained and the complex plane, Bode and admittance plots are displayed in Fig. 2.21.

Table 2.9. Calculations of the impedance, modulus, phase angle and admittances.

	A	B	C	D	E	F	G	H
1	Rs=	10	C=	2.00E-05	R=	100		
2								
3	log(om)	om	Z'	Z"	Y'	Y"	log|Z|	phi
4	-4	0.0001	1.10E+02	-2.00E-05	9.09E-03	1.65E-09	2.04E+00	-1.04E-05
5	-3.9	0.000126	1.10E+02	-2.52E-05	9.09E-03	2.08E-09	2.04E+00	-1.31E-05
6	-3.8	0.000158	1.10E+02	-3.17E-05	9.09E-03	2.62E-09	2.04E+00	-1.65E-05
7	-3.7	0.0002	1.10E+02	-3.99E-05	9.09E-03	3.30E-09	2.04E+00	-2.08E-05
8	-3.6	0.000251	1.10E+02	-5.02E-05	9.09E-03	4.15E-09	2.04E+00	-2.62E-05
9	-3.5	0.000316	1.10E+02	-6.32E-05	9.09E-03	5.23E-09	2.04E+00	-3.29E-05
10	-3.4	0.000398	1.10E+02	-7.96E-05	9.09E-03	6.58E-09	2.04E+00	-4.15E-05
11	-3.3	0.000501	1.10E+02	-1.00E-04	9.09E-03	8.28E-09	2.04E+00	-5.22E-05
12	-3.2	0.000631	1.10E+02	-1.26E-04	9.09E-03	1.04E-08	2.04E+00	-6.57E-05
13	-3.1	0.000794	1.10E+02	-1.59E-04	9.09E-03	1.31E-08	2.04E+00	-8.27E-05
14	-3	0.001	1.10E+02	-2.00E-04	9.09E-03	1.65E-08	2.04E+00	-1.04E-04
15	-2.9	0.001259	1.10E+02	-2.52E-04	9.09E-03	2.08E-08	2.04E+00	-1.31E-04
16	-2.8	0.001585	1.10E+02	-3.17E-04	9.09E-03	2.62E-08	2.04E+00	-1.65E-04
17	-2.7	0.001995	1.10E+02	-3.99E-04	9.09E-03	3.30E-08	2.04E+00	-2.08E-04
18	-2.6	0.002512	1.10E+02	-5.02E-04	9.09E-03	4.15E-08	2.04E+00	-2.62E-04
19	-2.5	0.003162	1.10E+02	-6.32E-04	9.09E-03	5.23E-08	2.04E+00	-3.29E-04
20	-2.4	0.003981	1.10E+02	-7.96E-04	9.09E-03	6.58E-08	2.04E+00	-4.15E-04
21	-2.3	0.005012	1.10E+02	-1.00E-03	9.09E-03	8.28E-08	2.04E+00	-5.22E-04

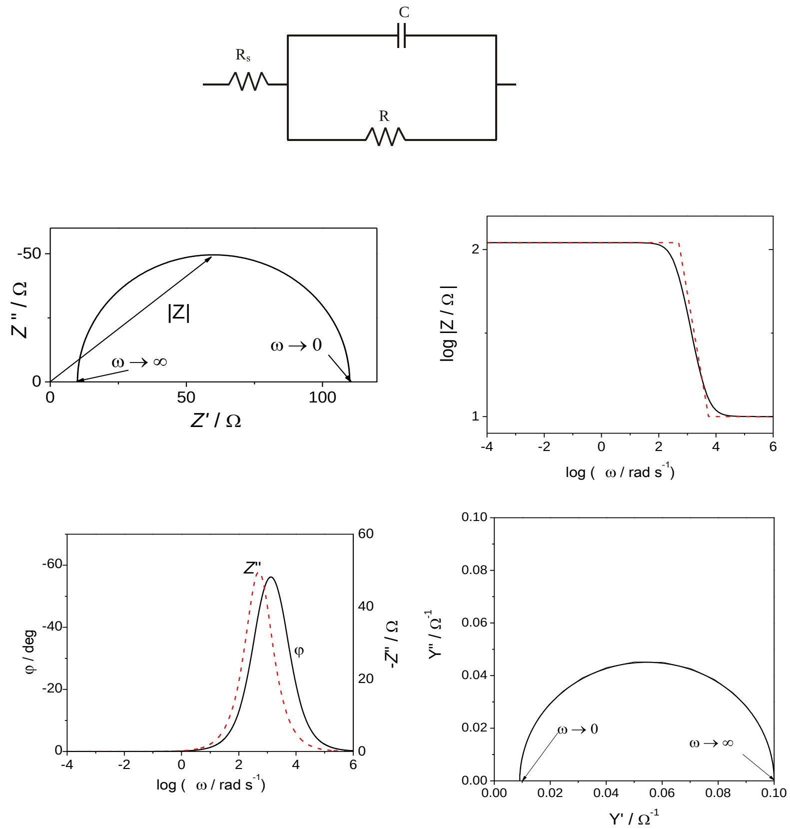


Fig. 2.21. Complex plane impedance, Bode, and complex plane admittance plots for the resistance R_s with the connection of R and C in parallel, $R_s = 10\ \Omega$, $R = 100\ \Omega$, $C = 20\ \mu F$.

The complex plane plot represents a semicircle shifted to higher values by a constant resistance R_s =10 Ω. The high frequency current flows through the capacitance C and the total impedance is real equal to R_s. The dc current (ω = 0) flows through R_s and R and the impedance is real equal equal to $R_s + R = 110\ \Omega$.

The phase angle is:

$$\varphi = \operatorname{atan}\left(\frac{Z''}{Z'}\right) = \operatorname{atan}\left[\frac{\omega R^2 C}{R_s + R + R_s(\omega RC)^2}\right] \tag{2.16}$$

and the maximum of the phase angle is observed at the frequency:

$$\omega_{\max} = \frac{1}{RC}\sqrt{\frac{R_s}{R}+1} \tag{2.17}$$

which in this example appears at $\omega_{\max} = 1658\ \mathrm{rad\ s^{-1}}$. One can notice that the maximum of the phase angle appears at the frequency higher than the maximum of the imaginary part of the semicircle, which is at $\omega_{\max,\mathrm{Im}} = 1/RC = 500\ \mathrm{rad\ s^{-1}}$, as in the simple RC parallel circuit. This is schematically displayed in Fig. 2.22, Bode phase angle. The value of $\omega_{\max}$ approaches that of $\omega_{\max,\mathrm{Im}}$ when $R_s / R \ll 1$, that is when the series resistance R_s is very small.

Exercise 2.12.

Make complex plane and Bode plots for the circuit $R_s(C_{dl}(R_{ct}C_p))$ with the following elements: $R_s = 2\ \Omega$, $R_{ct} = 50\ \Omega$, $C_{dl} = 2\times10^{-5}\ \mathrm{F}$, and $C_p = 0.01\ \mathrm{F}$.

The impedance of the system is easily written as:

$$\hat{Z} = R_s + \cfrac{1}{j\omega C_{dl} + \cfrac{1}{R_{ct} + \cfrac{1}{j\omega C_p}}} \tag{2.18}$$

The total impedance can be separated into the real and imaginary parts although the calculations are laborious and it is easily to make a mistake. It can be done easily in Maple:

```
> Z:=Rs+1/(I*om*Cdl+1/(Rct+1/(I*om*Cp)));
```

$$Z := Rs + \cfrac{1}{I\ om\ Cdl + \cfrac{1}{Rct - \cfrac{I}{om\ Cp}}}$$

```
> Z1:=simplify(Z);
```

$$Z1 := \frac{I\ Rs\ om^2\ Cdl\ Rct\ Cp + Rs\ om\ Cdl + Rs\ om\ Cp + Rct\ om\ Cp - I}{om\ (I\ Cdl\ Rct\ om\ Cp + Cdl + Cp)}$$

```
> ReZ1:=simplify(evalc(Re(Z1)));
```

$$ReZ1 := \frac{Rs\ Cdl^2 + 2\ Rs\ Cdl\ Cp + Rs\ Cp^2 + Rct\ Cp^2 + Cdl^2\ Rct^2\ Cp^2\ Rs\ om^2}{Cdl^2 + 2\ Cdl\ Cp + Cp^2 + Cdl^2\ Rct^2\ om^2\ Cp^2}$$

```
> ImZ1:=simplify(evalc(Im(Z1)));
```

$$ImZ1 := -\frac{Cdl + Cp + om^2\,Cdl\,Rct^2\,Cp^2}{om\,(Cdl^2 + 2\,Cdl\,Cp + Cp^2 + Cdl^2\,Rct^2\,om^2\,Cp^2)}$$

As we can see although the expressions for the real and imaginary parts are relatively complicated, they could be implemented in Excel. However, much simpler method is to calculate the impedances and admittances of different parts of the circuit starting from the deepest:

$$\begin{aligned}
\hat{Z}_{\mathrm{f}} &= R_{\mathrm{ct}} + \frac{1}{j\omega C_{\mathrm{p}}} = R_{\mathrm{ct}} - j\frac{1}{\omega C_{\mathrm{p}}} \\
\hat{Y}_{\mathrm{f}} &= \frac{1}{\hat{Z}_{\mathrm{f}}} \\
\hat{Y}_{\mathrm{el}} &= \hat{Y}_{\mathrm{f}} - j\frac{1}{\omega C_{\mathrm{dl}}} \\
\hat{Z}_{\mathrm{el}} &= \frac{1}{\hat{Y}_{\mathrm{el}}} \\
\hat{Z} &= R_{\mathrm{s}} + \hat{Z}_{\mathrm{el}}
\end{aligned} \tag{2.19}$$

keeping in mind that inversion of complex numbers is calculated as:

$$\frac{1}{a + jb} = \left(\frac{a}{a^2 + b^2}\right) - j\left(\frac{b}{a^2 + b^2}\right) \tag{2.20}$$

The results of calculations are shown in Excel file Ch2.xlsx Worksheet Ex2.11 and in Table 2.10.

Table 2.10. Calculations of the impedance, modulus, phase angle and admittances for Exercise 2.12

	A	B	C	D	E	F	G	H	I	J	K	L
1	Rs=	2	Cdl=	2.00E-05	Rct=	50	Cp=	1.00E-02				
2												
3	log(om)	om	Zf'	Zf"	Yf'	Yf"	Yel'	Yel"	Z'el	Z"el	Ztotal'	Ztotal"'
4	-4	1E-04	50	-1.00E+06	5.00E-11	1.00E-06	5.00E-11	1.00E-06	4.98E+01	-9.98E+05	5.18E+01	-9.98E+05
5	-3.9	1E-04	50	-7.94E+05	7.92E-11	1.26E-06	7.92E-11	1.26E-06	4.98E+01	-7.93E+05	5.18E+01	-7.93E+05
6	-3.8	2E-04	50	-6.31E+05	1.26E-10	1.58E-06	1.26E-10	1.59E-06	4.98E+01	-6.30E+05	5.18E+01	-6.30E+05
7	-3.7	2E-04	50	-5.01E+05	1.99E-10	2.00E-06	1.99E-10	2.00E-06	4.98E+01	-5.00E+05	5.18E+01	-5.00E+05
8	-3.6	3E-04	50	-3.98E+05	3.15E-10	2.51E-06	3.15E-10	2.52E-06	4.98E+01	-3.97E+05	5.18E+01	-3.97E+05
9	-3.5	3E-04	50	-3.16E+05	5.00E-10	3.16E-06	5.00E-10	3.17E-06	4.98E+01	-3.16E+05	5.18E+01	-3.16E+05
10	-3.4	4E-04	50	-2.51E+05	7.92E-10	3.98E-06	7.92E-10	3.99E-06	4.98E+01	-2.51E+05	5.18E+01	-2.51E+05
11	-3.3	5E-04	50	-2.00E+05	1.26E-09	5.01E-06	1.26E-09	5.02E-06	4.98E+01	-1.99E+05	5.18E+01	-1.99E+05
12	-3.2	6E-04	50	-1.58E+05	1.99E-09	6.31E-06	1.99E-09	6.32E-06	4.98E+01	-1.58E+05	5.18E+01	-1.58E+05
13	-3.1	8E-04	50	-1.26E+05	3.15E-09	7.94E-06	3.15E-09	7.96E-06	4.98E+01	-1.26E+05	5.18E+01	-1.26E+05
14	-3	0.001	50	-1.00E+05	5.00E-09	1.00E-05	5.00E-09	1.00E-05	4.98E+01	-9.98E+04	5.18E+01	-9.98E+04
15	-2.9	0.001	50	-7.94E+04	7.92E-09	1.26E-05	7.92E-09	1.26E-05	4.98E+01	-7.93E+04	5.18E+01	-7.93E+04
16	-2.8	0.002	50	-6.31E+04	1.26E-08	1.58E-05	1.26E-08	1.59E-05	4.98E+01	-6.30E+04	5.18E+01	-6.30E+04
17	-2.7	0.002	50	-5.01E+04	1.99E-08	2.00E-05	1.99E-08	2.00E-05	4.98E+01	-5.00E+04	5.18E+01	-5.00E+04
18	-2.6	0.003	50	-3.98E+04	3.15E-08	2.51E-05	3.15E-08	2.52E-05	4.98E+01	-3.97E+04	5.18E+01	-3.97E+04
19	-2.5	0.003	50	-3.16E+04	5.00E-08	3.16E-05	5.00E-08	3.17E-05	4.98E+01	-3.16E+04	5.18E+01	-3.16E+04
20	-2.4	0.004	50	-2.51E+04	7.92E-08	3.98E-05	7.92E-08	3.99E-05	4.98E+01	-2.51E+04	5.18E+01	-2.51E+04
21	-2.3	0.005	50	-2.00E+04	1.26E-07	5.01E-05	1.26E-07	5.02E-05	4.98E+01	-1.99E+04	5.18E+01	-1.99E+04
22	-2.2	0.006	50	-1.58E+04	1.99E-07	6.31E-05	1.99E-07	6.32E-05	4.98E+01	-1.58E+04	5.18E+01	-1.58E+04
23	-2.1	0.008	50	-1.26E+04	3.15E-07	7.94E-05	3.15E-07	7.96E-05	4.98E+01	-1.26E+04	5.18E+01	-1.26E+04
24	-2	0.01	50	-1.00E+04	5.00E-07	1.00E-04	5.00E-07	1.00E-04	4.98E+01	-9.98E+03	5.18E+01	-9.98E+03

Looking at the circuit it is evident that the dc current cannot flow through it because the two parallel branches are blocked by capacitances. This means, that the low frequency imaginary impedance part must go to negative infinity.

On the other hand, at very high frequencies the capacitances do not obstruct current flow (impedance of the capacitor goes to zero) and the total ac current flows through R_s and the upper branch, therefore the impedance is R_s. In the medium frequencies the coupling of R_{ct} and C_{dl} produces a semicircle with the time constant $\tau = R_{ct}C_{dl} = 1\ \text{ms}$. On the Bode plots a semicircle produces as S shaped wave (corresponding to the semicircle) followed by a straight line with a slope of -1. The phase angle plot shows a peak at higher frequencies, corresponding to the semicircle and then the phase angle goes to -90° as the imaginary part of the impedance goes to -∞. On the complex admittance at high frequencies the admittance is $1/2\,\Omega = 0.5\,\Omega^{-1}$, at low frequencies it goes to zero as impedance goes to -∞. Two semicircles are observed on the complex admittance plots. The radius of the small low frequency semicircle corresponds to $1/(R_s + R_{ct}) = 1/52\,\Omega^{-1}$, which is the total low frequency real resistance at the complex impedance plots.

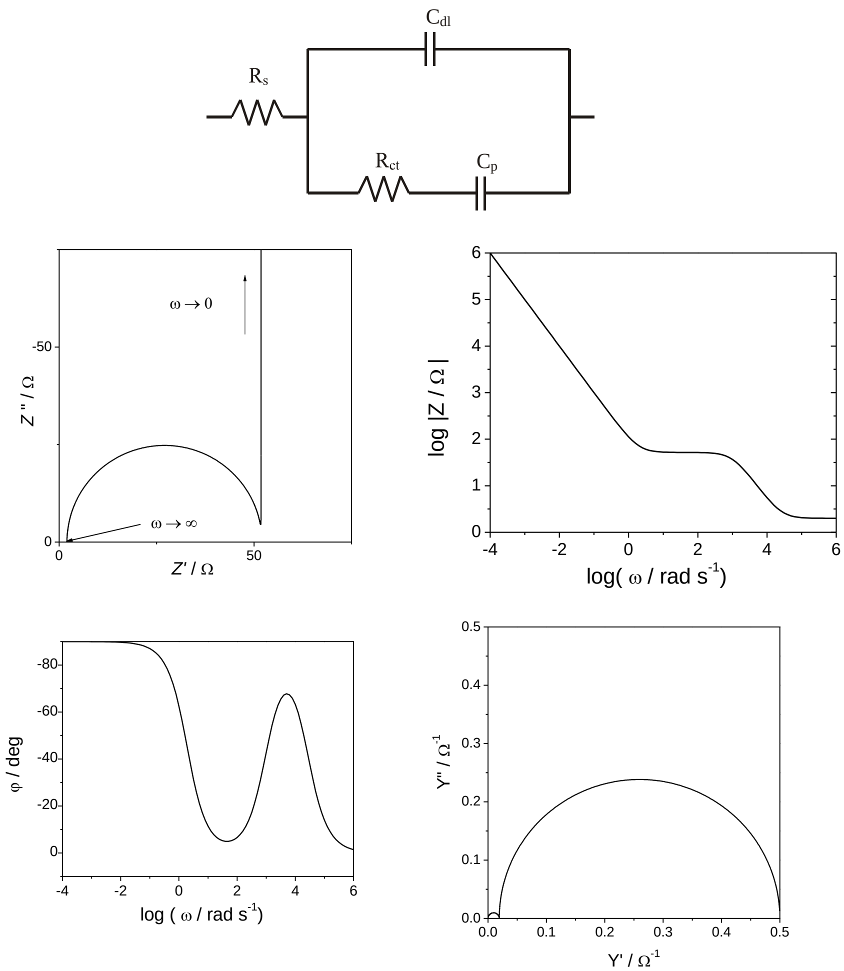


Fig. 2.22. Complex plane impedance, Bode, and complex plane admittance plots for the resistance R_s with the connection of R and C in parallel, $R_s = 2\ \Omega$, $R_{ct} = 50\ \Omega$, $C_{dl} = 20\ \mu F$, $C_p = 0.01$ F.

Exercise 2.13.

Simulate using ZView impedance of the two models displayed in Fig. 2.37, book, series $R_0(R_1C_1)(R_2C_2)$ and nested $R_0(C_1(R_1(R_2C_2)))$, using the following parameters: $R_s = 10\ \Omega$, $R_1 = 100\ \Omega$, $C_1 = 2\times10^{-5}$ F, $R_2 = 100\ \Omega$, $C_2 = 10^{-1}$, 10^{-3},

10^{-4}, 2×10^{-5}, 10^{-5} F. Make the approximations of the impedances of the nested circuit by that in series. Compare with the results in Ch2.xlsx, Worksheets Ex2.13 serial, Ex2.13 nested, and Ex2.13 approx.

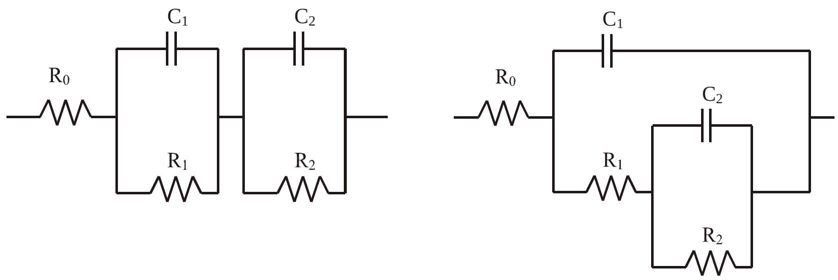
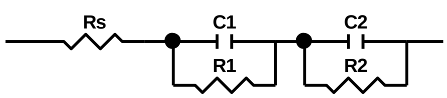


Fig. 2.23. Two circuits producing two semicircles on the complex plane plots; left – Voigt (is series), right – nested.

First build these circuits in ZView. An Example of such circuit is shown in Fig. 2.24. Then simulate impedances between 10^{-5} and 10^{5} Hz, copy the results into clipboard and then paste them to Excel. Make the complex plane and Bode plots. Compare your results with the Excel files: Ch2.xlsx, Worksheet Ex2.13 serial and Ex2.13 nested, and plots in Fig. 2.25 and 2.26.

Make approximations of the impedances simulated using the nested circuit by the one containing two parallel RC in series, Fig. 2.23, left. Compare the obtained results with those in Table 2.11 and Worksheet Ex2.13 approx.



Element	Freedom	Value	Error	Error %
Rs	Fixed(X)	10	N/A	N/A
C1	Fixed(X)	2E-05	N/A	N/A
R1	Fixed(X)	100	N/A	N/A
C2	Fixed(X)	0.01	N/A	N/A
R2	Fixed(X)	100	N/A	N/A

Data File:	
Circuit Model File:	
Mode:	Run Simulation / Freq. Range (1E-5 - 10
Maximum Iterations:	100
Optimization Iterations:	0
Type of Fitting:	Complex
Type of Weighting:	Calc-Modulus

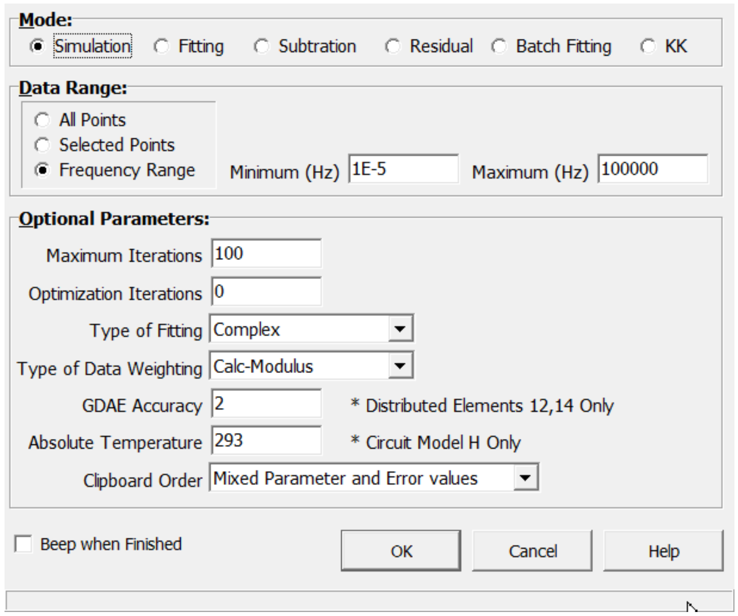


Fig. 2.24. Voigt circuit built in ZView and ready for simulations.

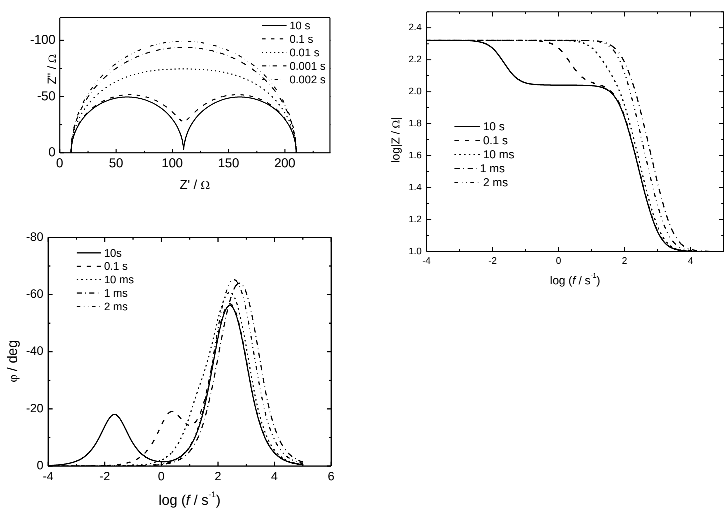


Fig. 2.25. Complex plane and Bode plots for a series circuit in Fig. 2.23, left.

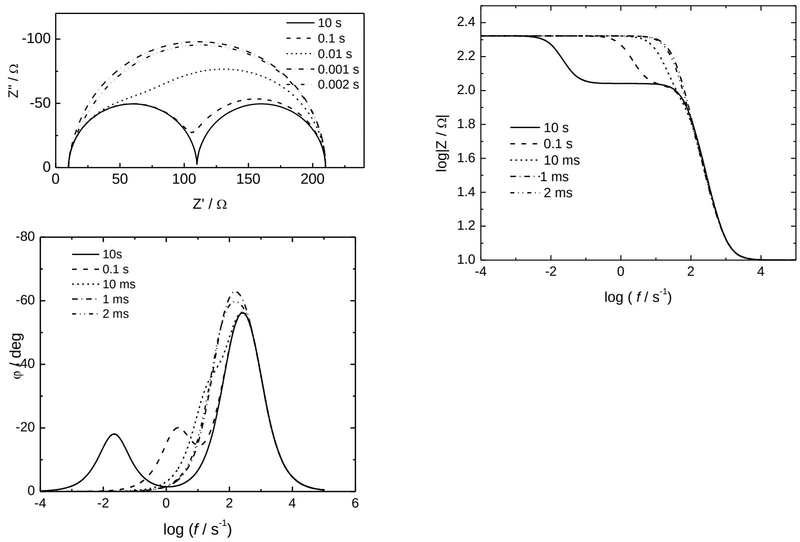


Fig. 2.26. Complex plane and Bode plots a nested circuit for Fig. 2.23, right. The numbers indicate the time constants of the second (*RC*) circuit.

Table 2.11. Results of the fit of impedances in Fig. 2.26 to the circuit containing two parallel (*RC*) elements in series. : $R_0 = 10\ \Omega$, $R_1 = R_2 = 100\ \Omega$, $C_1 = 20\ \mu\text{F}$ **and different assumed values of C_2 indicated below; the parameters found using fit to the series circuit are indicated.**

C_2 assumed / F	R_1 found / Ω	C_1 found / F	R_2 found / Ω	C_2 found / F
0.100	99.96	2.00×10^{-5}	100.0	1.53×10^{-6}
1.00×10^{-3}	96.00	2.04×10^{-5}	104.0	1.35×10^{-8}
1.00×10^{-4}	62.86	2.57×10^{-5}	137.1	1.54×10^{-9}
2.00×10^{-5}	10.56	7.24×10^{-5}	189.4	3.02×10^{-10}
1.00×10^{-5}	2.99	1.47×10^{-4}	197.0	1.57×10^{-10}

Exercise 2.14.

Simulate impedances for the circuit *RCL* in series for $R = 1\ \Omega$, $C = 0.01$ F, and $L = 0.01$ H. Make simulations using ZView and Excel. Make complex plane and Bode plots.

The results are shown in the Excel file Ch2.xlsx Worksheet Ex2.14.

Exercise 3.1.

Simulate sum of odd harmonic functions: $\sum A_i \cos(2\pi v_i t + \pi b_i)$ for:

Frequencies, v / Hz

1 3 5 7 9 11 13 17 21 25 31 37 44 52 64 75 90 100 110 130 170 210 250 310 370 440 520 640 750 900 1000

Relative amplitudes, A:

0.25	0.1796024	0.154003	0.1391682	0.1290281	0.1214646	0.1155073	0.1065462
0.09997981	0.09486765	0.08891917	0.08430711	0.08002237	0.0760977	0.07148676	0.06815384
0.06451406	0.0625	0.06073228	0.05775367	0.0532731	0.04998991	0.04743382	0.04445958
0.04215356	0.04001119	0.03804884	0.03574338	0.03407692	0.03225703	0.03125	

Relative phases, b, $\varphi = \pi * b$

0.7055475	0.533424	0.5795186	0.2895625	0.301948	0.7747401
0.01401764	0.7607236	0.81449	0.7090379	0.04535276	0.4140327
0.8626193	0.79048	0.3735362	0.9619532	0.8714458	0.05623686
0.9495566	0.3640187	0.5248684	0.7671117	0.05350453	0.5924582
0.4687001	0.2981654	0.6226967	0.6478212	0.2637929	0.2793421
0.8298016					

Make the simulations for the total time of one second for $N = 2048$ points, that is for $\Delta t = 1/2048$ s. Calculate the Fourier transform of this function and its amplitude (modulus) versus frequency up to the Nyquist. The results are in file Ch3.xlsx. The calculated function is displayed in Fig. 3.1.

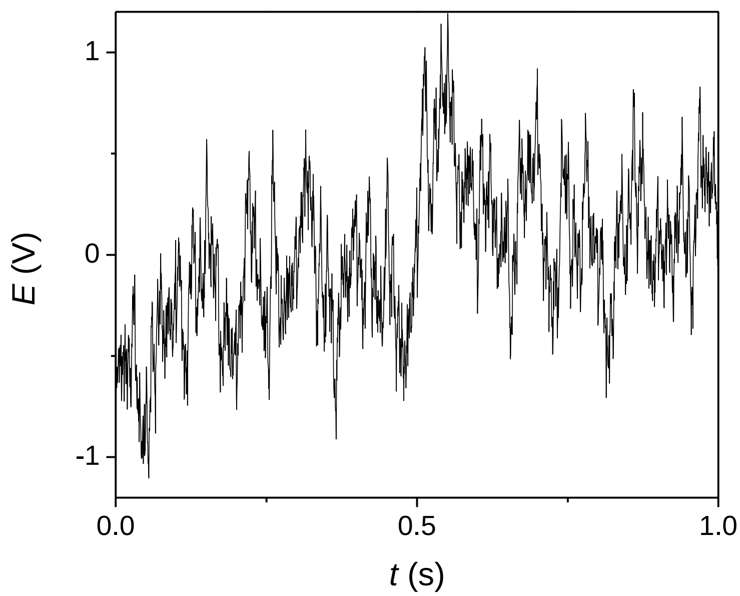


Fig. 3.1. Plot of the function in Exercise 3.1.

The Fourier transform of this function was calculated in Excel. The plot of the amplitude |*E*| versus frequency (up to the Nyquist frequency) is shown in Fig. 3.2. As recommended, the amplitudes of the odd harmonics decrease with frequency.

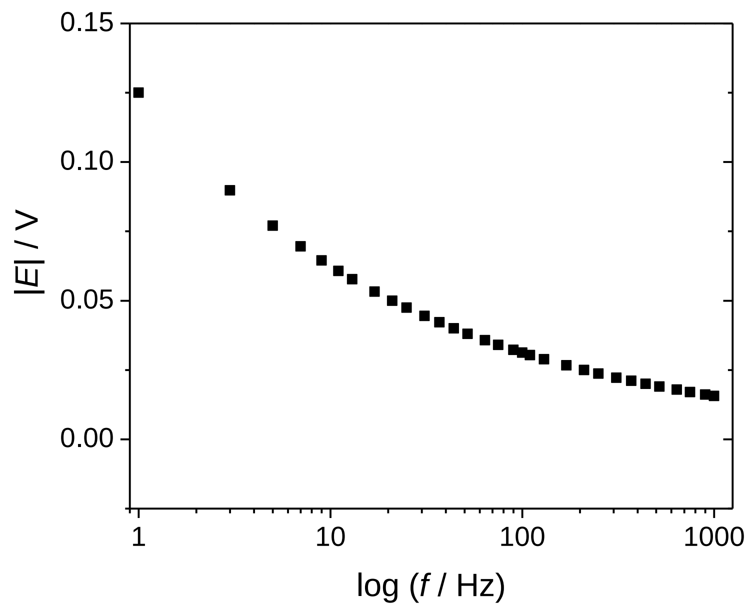


Fig. 3.2. Fourier transform of the function in Fig. 3.1.

Exercise 4.1.

Write a program in Maple or Mathematica for the Randles model and make the corresponding complex plane and Bode plots.

An example of the Maple program is shown below. In the directory there are two programs: 4-1.mw and 4-1.nb as well as the obtained data files Randles.txt.

> *restart*;

> $\text{sigma} := \frac{R \cdot T}{\left(F^2 \cdot Co \cdot \text{sqrt}(Do)\right)}$;

$$\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$$

> $Zw := \frac{4 \cdot \text{sigma}}{\text{sqrt}(I \cdot \text{omega})}$;

$$Zw := \frac{4\,R\,T}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}$$

> $Zf := Rct + Zw$;

$$Zf := Rct + \frac{4\,R\,T}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}$$

> $Z := Rs + \frac{1}{\frac{1}{Zf} + I \cdot \text{omega} \cdot Cdl}$;

$$Z := Rs + \frac{1}{\frac{1}{Rct + \frac{4\,R\,T}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}} + \mathrm{I}\,\omega\,Cdl}$$

> $Z1 := \text{Re}(Z)$;

$$Z1 := \Re\left(Rs + \frac{1}{\frac{1}{Rct + \frac{4\,R\,T}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}} + \mathrm{I}\,\omega\,Cdl}\right)$$

> $Z2 := \text{Im}(Z)$;

$$Z2 := \Im\left(Rs + \frac{1}{\frac{1}{Rct + \frac{4\,R\,T}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}} + \mathrm{I}\,\omega\,Cdl}\right)$$

> $ZM := \text{sqrt}\left(Z1^2 + Z2^2\right)$;

> $\text{omega} := 10^{lom}$;

$$\omega := 10^{lom}$$

> $Rs := 10$;

$$Rs := 10$$

> $Cdl := 20\text{e}-6$;

$$Cdl := 0.000020$$

> $Do := 1\text{e}-5$;

$$Do := 0.00001$$

> $F := 96485$;

$$F := 96485$$

> $T := 298.15$;

$$T := 298.15$$

> $R := 8.31447;$

$$R := 8.31447$$

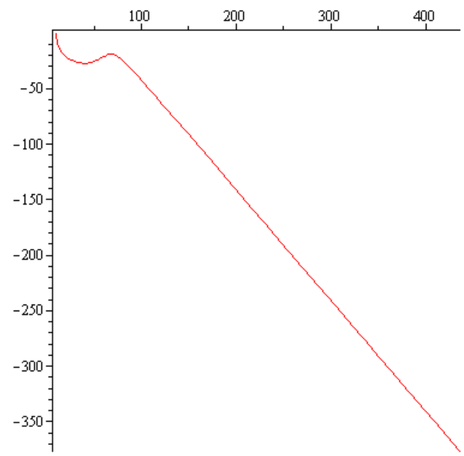
> $Rct := 50;$

$$Rct := 50$$

> $Co := 2e-6;$

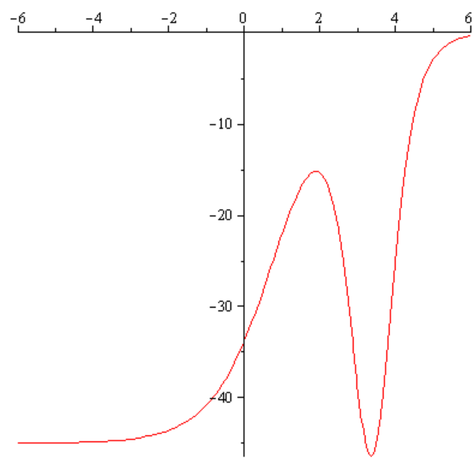
$$Co := 0.000002$$

> $plot([Z1, Z2, lom = -1..5]);$



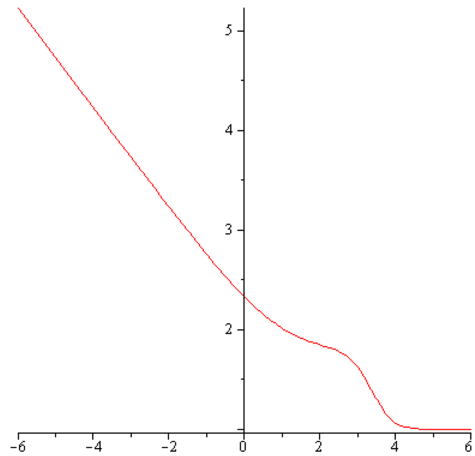
> $\varphi := \frac{\arctan\left(\frac{Z2(lom)}{Z1(lom)}\right) \cdot 180}{\text{Pi}};$

> $plot([lom, \varphi, lom = -6..6]);$



> $lZM := \log10(ZM);$

> $plot([lom, lZM, lom = -6..6]);$



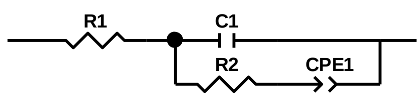

```
> filenamebase := "Randles";
                              filenamebase := "Randles
> filename := cat(currentdir( ), "\\", filenamebase, ".txt") :
>
  dat := NULL :
  for lom from −2 to 7 by 0.1 do
  dat := dat, [lom, Z1(lom), Z2(lom)];
  end do:
  dat := evalf([dat]) :

> writedata(filename, dat, float);
```

Exercise 4.2.

Construct the model of the Randles' circuit in ZView, Fig. 4.2 (book): $R_s(C_{dl}(R_{ct}Z_W)$, and make the simulation using data: R_s = 10 Ω, C_{dl} = 25 μF, R_{ct} = 50 Ω, σ' = 10 Ω $s^{-1/2}$. Repeat simulations in Maple or Mathematica.

The following model should be constructed:



Element	Freedom	Value	Error	Error %
R1	Fixed(X)	10	N/A	N/A
C1	Fixed(X)	2.5E-05	N/A	N/A
R2	Fixed(X)	50	N/A	N/A
CPE1-T	Fixed(X)	0.1	N/A	N/A
CPE1-P	Fixed(X)	0.5	N/A	N/A

Fig. 4.1. Model $R_1(C_1(R_2C_2)$ in ZView.

To represent the Warburg impedance one should use so called constant phase element (see Chapter 7). Its impedance is described in this particular case as:

$$\hat{Z}_{\mathrm{CPE}} = \frac{1}{(j\omega)^P T} = \frac{1}{(j\omega)^{0.5} T} \tag{4.1}$$

where simply $\sigma' = 1/T$. Using this circuit the complex plane and Bode plots are as shown in Fig. 4.2 (book).

Similar simulation can be simply carried out in Maple or Mathematica, see file, 4-2.mw and 4-2.nb.

> *restart*

> $Zt := Rs + \frac{1}{\frac{1}{Rct + \frac{\sigma}{(I \cdot \omega)^{0.5}}} + I \cdot \omega \cdot Cdl}$

$$Zt := Rs + \frac{1}{\frac{1}{Rct + \frac{\sigma}{(\mathrm{I}\,\omega)^{0.5}}} + \mathrm{I}\,\omega\,Cdl}$$

> $Rs := 10$

$$Rs := 10$$

> $Rct := 50$

$$Rct := 50$$

>

> $Cdl := 0.000025$

$$Cdl := 0.000025$$

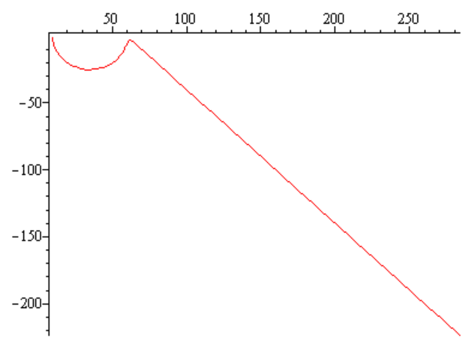
> $\sigma := 10$

$$\sigma := 10$$

> $\omega := 10^{lom}$

$$\omega := 10^{lom}$$

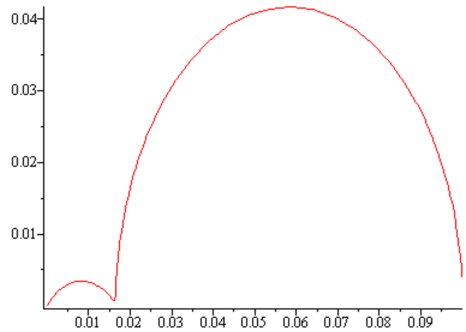
> $plot([\mathrm{Re}(Zt(lom)), \mathrm{Im}(Zt(lom)), lom = -3..5])$



> $Yt := \frac{1}{Zt}$

$$Yt := \frac{1}{10 + \frac{1}{\frac{1}{50 + \frac{10}{(\mathrm{I}\,10^{lom})^{0.5}}} + 0.000025\,\mathrm{I}\,10^{lom}}}$$

> $plot([\mathrm{Re}(Yt(lom)), \mathrm{Im}(Yt(lom)), lom = -6..5])$




```
> filenamebase := "Randles2"
                    filenamebase := "Randles2"
> filename := cat(currentdir( ), "\\", filenamebase, ".txt") :
>
  dat := NULL :
  for lom from −2 to 7 by 0.1 do
  dat := dat, [lom, Re(Zt(lom)), Im(Zt(lom))];
  end do:
  dat := evalf([dat]) :

> writedata(filename, dat, float);
```

Exercise 4.3.

Write a Maple/Mathematica programs to simulate spherical internal diffusion and the corresponding complex plane and Bode plots using the following parameters: R_s=10 Ω, C_{dl}=2×10^{-5} F, D_O=10^{-5} cm^2 s^{-1}, R_{ct}=50 Ω, C_O=2×10^{-6} mol cm^{-3}, r_0=10^{-3} cm.

See solution in files 4-3.mw and 4-3.nb.

> restart

> $\sigma := \dfrac{R\,T}{F^2\,Co\,\sqrt{Do}}$;

$$\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$$

> $Zw := \dfrac{\sigma}{\sqrt{I\,\omega}\,\coth\left(\sqrt{\dfrac{I\,\omega}{Do}}\,r0\right) - \dfrac{\sqrt{Do}}{r0}}$;

$$Zw := \frac{R\,T}{F^2\,Co\,\sqrt{Do}\,\left(\sqrt{\mathrm{I}\,\omega}\,\coth\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\,r0\right) - \frac{\sqrt{Do}}{r0}\right)}$$

> $Zf := Rct + Zw$

$$Zf := Rct + \frac{R\,T}{F^2\,Co\,\sqrt{Do}\,\left(\sqrt{\mathrm{I}\,\omega}\,\coth\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\,r0\right) - \frac{\sqrt{Do}}{r0}\right)}$$

> $Z := Rs + \dfrac{1}{\dfrac{1}{Zf} + I\,\omega\,Cdl}$

> $Z1 := \mathrm{Re}(Z)$

> $Z2 := \mathrm{Im}(Z)$

> $ZM := \sqrt{Z1^2 + Z2^2}$

> $\omega := 10^{lom}$

$$\omega := 10^{lom}$$

> $Rs := 10$

$$Rs := 10$$

> $Cdl := 0.00002$

$$Cdl := 0.00002$$

> $Do := 0.00001$

$$Do := 0.00001$$

> $F := 96485$

$$F := 96485$$

> $T := 298.15$

$$T := 298.15$$

> $R := 8.31447$

$$R := 8.31447$$

> $Rct := 50$

$$Rct := 50$$

> $Co := 2e\text{-}6$

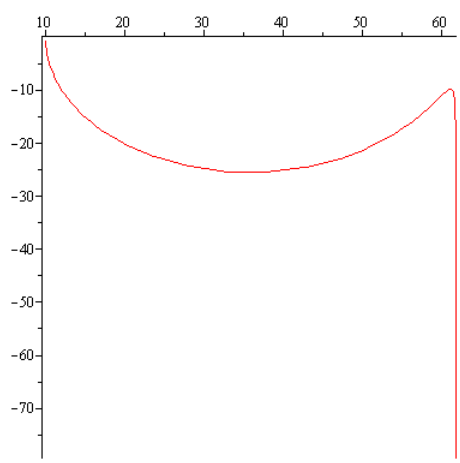
$$Co := 0.000002$$

> $r0 := 0.001$

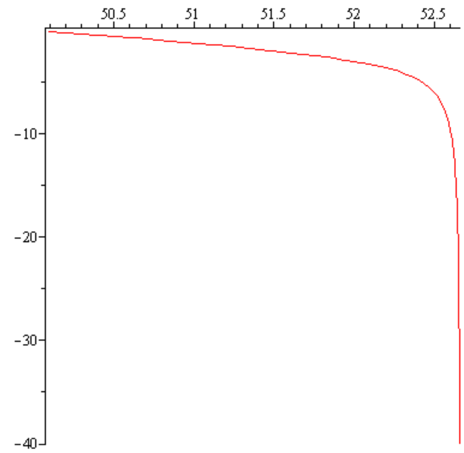
$$r0 := 0.001$$

>

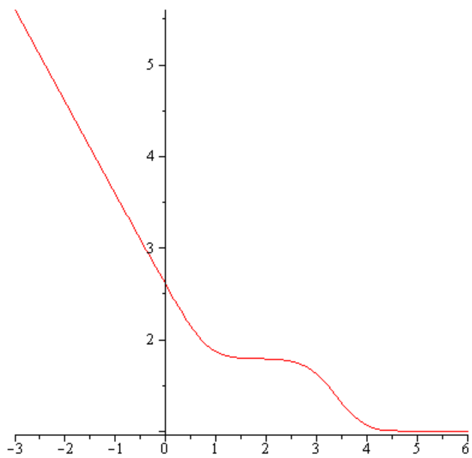
> $plot([Z1, Z2, lom = 0.7 ..5])$



> $plot([\Re(Zf), \Im(Zf), lom = 1 ..5])$

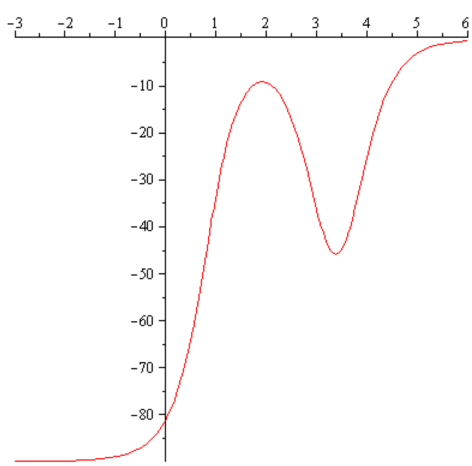


> $plot([lom, \log10(ZM), lom = -3..6])$



> $\phi := \frac{\arctan\left(\frac{Z2}{Z1}\right) \cdot 180}{\pi}$

> $plot([lom, \phi, lom = -3..6])$



> *filenamebase* := "spherint-Maple

filenamebase := "spherint-Maple

> $filename := cat(currentdir(\ ), "\backslash\backslash", filenamebase, ".txt")$

$$filename := "D:\backslash doc\backslash EIS\backslash Exercises\backslash Ch4\backslash spherint\text{-}Maple.t$$

>
```
dat := NULL :
for lom from −2 to 6 by 0.1 do
dat := dat, [lom, Z1(lom), Z2(lom)]
end do:
dat := evalf([dat]) :
```

> $writedata(filename, dat, float);$

Exercise 4.4.

Write a program in Maple or Mathematica to simulate semi-infinite spherical fusion (external) diffusion and create the corresponding complex plane and Bode plots. The parameters as in Exercise 4.3 except r_0=0.01 cm.

See solution in files 4-4.mw and 4-4.nb. The Maple file is shown below.

> $restart$

> $\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$

$$\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$$

> $Zw := \frac{2\,\sigma}{\sqrt{I\,\omega} + \frac{\sqrt{Do}}{r0}}$

$$Zw := \frac{2\,R\,T}{F^2\,Co\,\sqrt{Do}\left(\sqrt{\mathrm{I}\,\omega} + \frac{\sqrt{Do}}{r0}\right)}$$

> $Zf := Rct + Zw$

$$Zf := Rct + \frac{2\,R\,T}{F^2\,Co\,\sqrt{Do}\left(\sqrt{\mathrm{I}\,\omega} + \frac{\sqrt{Do}}{r0}\right)}$$

> $Z := Rs + \frac{1}{\frac{1}{Zf} + I\,\omega\,Cdl}$

$$Z := Rs + \frac{1}{\frac{1}{Rct + \frac{2\,R\,T}{F^2\,Co\,\sqrt{Do}\left(\sqrt{\mathrm{I}\,\omega} + \frac{\sqrt{Do}}{r0}\right)}} + \mathrm{I}\,\omega\,Cdl}$$

> $Z1 := \Re(Z)$

> $Z2 := \Im(Z)$

> $ZM := \sqrt{Z1^2 + Z2^2}$

> $\omega := 10^{lom}$

$$\omega := 10^{lom}$$

> $Rs := 10$

$$Rs := 10$$

> $Cdl := 0.000020$

$$Cdl := 0.000020$$

> $Do := 0.00001$

$$Do := 0.00001$$

> $F := 96485$

$$F := 96485$$

> $T := 298.15$

$$T := 298$$

> $R := 8.31447$

$$R := 8.31447$$

> $Rct := 50$

$$Rct := 50$$

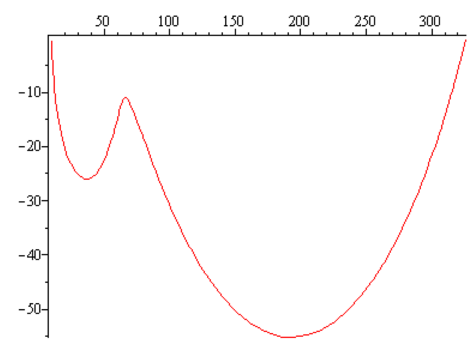
> $Co := 0.000002$

$$Co := 0.000002$$

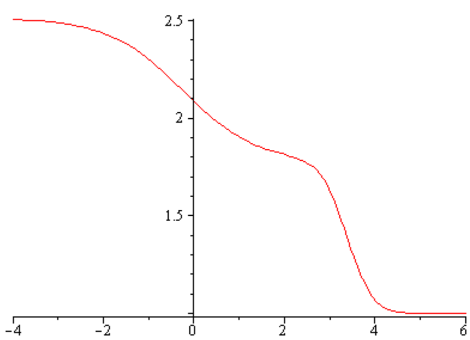
> $r0 := 0.01$

$$r0 := 0.01$$

> $plot([Z1, Z2, lom = -7..5])$

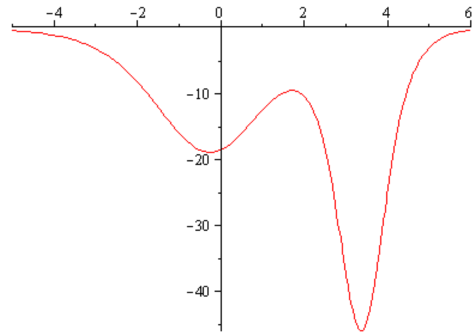


> $plot([lom, \log10(ZM), lom = -4..6])$



> $$\phi := \frac{\arctan\left(\frac{Z2}{Z1}\right) \cdot 180}{\pi}$$

> $plot([lom, \phi, lom = -5..6])$



> *filenamebase* := "spherext-Maple

filenamebase := "spherext-Maple

> *filename* := *cat*(*currentdir*( ), "\", *filenamebase*, ".txt")

> *dat* := *NULL*;

dat := *evalf*([*dat*])

```
dat := NULL;
for lom from -2 by 0.1 to 6 do
    dat := dat, [lom, Z1(lom), Z2(lom)]
  end do;
dat := evalf([dat])
```

> *writedata*(*filename*, *dat*, *float*)

Exercise 4.5.

Write a program in Maple/Mathematica to simulate transmissive finite-length impedance and the corresponding complex plane and Bode plots. The parameters as in Exercise 4.3 with *l*=0.01 cm.

The results are in 4-5.mw and 4-5.nb.

> *restart*

> $\sigma := \dfrac{R\,T}{F^2\,Co\,\sqrt{Do}}$

$$\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$$

> $Zw := \dfrac{\sigma\ \tanh\left(\sqrt{\dfrac{I\,\omega}{Do}}\ l\right)}{\sqrt{I\,\omega}}$

$$Zw := \frac{R\,T\tanh\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\ l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}$$

> $Zf := Rct + Zw$

$$Zf := Rct + \frac{R\,T\tanh\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\ l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}$$

> $Z := Rs + \dfrac{1}{\dfrac{1}{Zf} + I\,\omega\,Cdl}$

$$Z := Rs + \frac{1}{\dfrac{1}{Rct + \dfrac{R\,T\tanh\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\ l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}} + \mathrm{I}\,\omega\,Cdl}$$

> $ZM := \sqrt{Z1^2 + Z2^2}$

$$ZM := \sqrt{Z1^2 + Z2^2}$$

> $Z1 := \mathrm{Re}(Z)$

$$Z1 := \Re\left(Rs + \frac{1}{\dfrac{1}{Rct + \dfrac{R\,T \tanh\left(\sqrt{\dfrac{I\,\omega}{Do}}\;l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{I\,\omega}}} + I\,\omega\,Cdl}\right)$$

> $Z2 := \mathrm{Im}(Z)$

$$Z2 := \Im\left(Rs + \frac{1}{\dfrac{1}{Rct + \dfrac{R\,T \tanh\left(\sqrt{\dfrac{I\,\omega}{Do}}\;l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{I\,\omega}}} + I\,\omega\,Cdl}\right)$$

- > $\omega := 10^{lom}$

$$\omega := 10^{lom}$$

- > $Rs := 10$

$$Rs := 10$$

– > $Cdl := 0.000020$

$$Cdl := 0.000020$$

> $Do := 0.00001$

$$Do := 0.00001$$

> $F := 96485$

$$F := 96485$$

> $T := 298.15$

$$T := 298.15$$

> $R := 8.31447$

$$R := 8.31447$$

> $Rct := 50$

$$Rct := 50$$

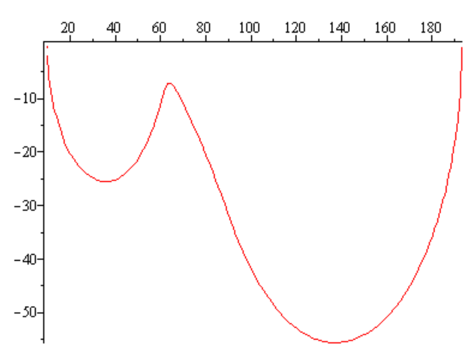
> $Co := 0.000002$

$$Co := 0.000002$$

> $l := 0.01$

$$l := 0.01$$

> $plot([Z1, Z2, lom = -3..6])$



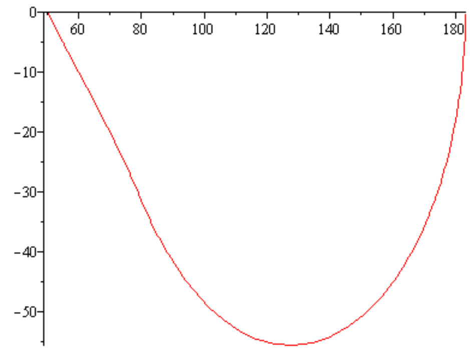
> $Zf1 := \mathrm{Re}(Zf)$

$$Zf1 := 50 + 42.10365382\, \Re\left(\frac{\tanh\left(0.01\sqrt{1.\,10^5\, \mathrm{I}\, 10^{lom}}\right)}{\sqrt{\mathrm{I}\, 10^{lom}}}\right)$$

> $Zf2 := \mathrm{Im}(Zf)$

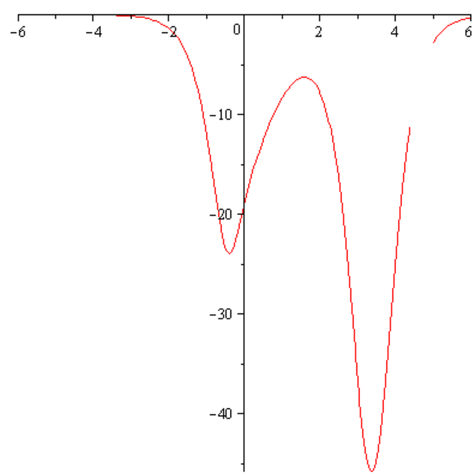
$$Zf2 := 42.10365382\, \Im\left(\frac{\tanh\left(0.01\sqrt{1.\,10^5\, \mathrm{I}\, 10^{lom}}\right)}{\sqrt{\mathrm{I}\, 10^{lom}}}\right)$$

> $plot([Zf1, Zf2, lom = -3..6])$



> $\phi := \frac{\arctan\left(\frac{Z2}{Z1}\right) \cdot 180}{\pi}$

> $plot([lom, \phi, lom = -6..6])$



> *filenamebase* := "FLtransm-Maple

filenamebase := "FLtransm-Maple

> *filename* := *cat*(*currentdir*( ), "\\", *filenamebase*, ".txt") :

```
>
 dat := NULL :
 for lom from -2 to 6 by 0.1 do
 dat := dat, [lom, Z1(lom), Z2(lom)];
 end do:
 dat := evalf([dat]) :
```

> *writedata*(*filename*, *dat*, *float*)

Exercise 4.6.

Write a program in Maple/Mathematica to simulate reflective finite-length impedance and the corresponding complex plane and Bode graphs. Use data as in Exercise 4.5.

Solution can be found in file 4-6.mw and 4-6.nb.

> *restart*

> $\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$

$$\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$$

> $Zw := \frac{\sigma\,\coth\left(\sqrt{\frac{I\,\omega}{Do}}\,l\right)}{\sqrt{I\,\omega}}$

$$Zw := \frac{R\,T\coth\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\,l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}$$

> $Zf := Rct + Zw$

$$Zf := Rct + \frac{R\,T\coth\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\,l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}$$

> $Z := Rs + \frac{1}{\frac{1}{Zf} + I\,\omega\,Cdl}$

$$Z := Rs + \frac{1}{\frac{1}{Rct + \frac{R\,T\coth\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\,l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}} + \mathrm{I}\,\omega\,Cdl}$$

> $ZM := \sqrt{Z1^2 + Z2^2}$

$$ZM := \sqrt{Z1^2 + Z2^2}$$

> $Z1 := \mathrm{Re}(Z)$

$$Z1 := \Re\left(Rs + \frac{1}{\frac{1}{Rct + \frac{R\,T\coth\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\,l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}} + \mathrm{I}\,\omega\,Cdl}\right)$$

> $Z2 := \mathrm{Im}(Z)$

$$Z2 := \Im\left(Rs + \frac{1}{\frac{1}{Rct + \frac{R\,T\coth\left(\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\,l\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}}} + \mathrm{I}\,\omega\,Cdl}\right)$$

- > $\omega := 10^{lom}$

$$\omega := 10^{lom}$$

- > $Rs := 10$

$$Rs := 10$$

– > $Cdl := 0.000020$

$$Cdl := 0.000020$$

> $Do := 0.00001$

$$Do := 0.00001$$

> $F := 96485$

$$F := 96485$$

> $T := 298.15$

$$T := 298.15$$

> $R := 8.31447$

$$R := 8.31447$$

> $Rct := 50$

$$Rct := 50$$

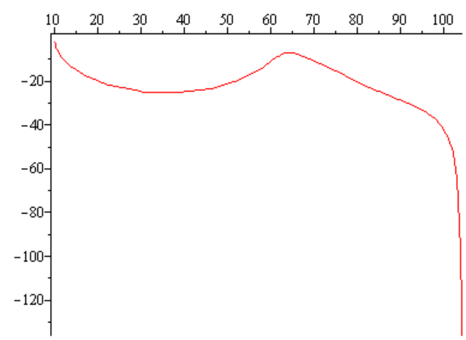
> $Co := 0.000002$

$$Co := 0.000002$$

> $l := 0.01$

$$l := 0.01$$

> $plot([Z1, Z2, lom = -1..6])$



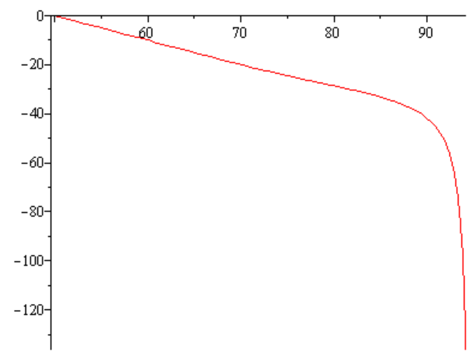
> $Zf1 := \mathrm{Re}(Zf)$

$$Zf1 := 50 + 42.10365382\, \Re\left(\frac{\coth\left(0.01\sqrt{1.\ 10^{5}\ \mathrm{I}\ 10^{lom}}\right)}{\sqrt{\mathrm{I}\ 10^{lom}}} \right)$$

> $Zf2 := \mathrm{Im}(Zf)$

$$Zf2 := 42.10365382\, \Im\left(\frac{\coth\left(0.01\sqrt{1.\ 10^{5}\ \mathrm{I}\ 10^{lom}}\right)}{\sqrt{\mathrm{I}\ 10^{lom}}} \right)$$

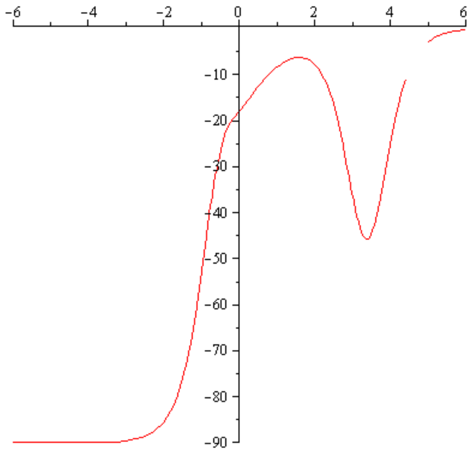
> $plot([Zf1, Zf2, lom = -1..6])$



```
> φ := arctan(Z2/Z1)·180/π
```

$$\phi := \frac{\arctan\left(\frac{Z2}{Z1}\right)\cdot 180}{\pi}$$

```
> plot([lom, φ, lom = -6..6])
```




```
> filenamebase := "FLreflect-Maple
```

filenamebase := "FLreflect-Maple

```
> filename := cat(currentdir( ), "\\", filenamebase, ".txt") :
>
  dat := NULL :
  for lom from -2 to 6 by 0.1 do
  dat := dat, [lom, Z1(lom), Z2(lom)];
  end do:
  dat := evalf([dat]) :

> writedata(filename, dat, float)
```

Exercise 4.7.

Write a Maple/Mathematica program to simulate cylindrical diffusion and the corresponding complex plane and Bode plots, use parameters as in Exercise 4.5 and r_0=0.01 cm.

Solution is found in file 4-7.mw and 4-7.nb.

> *restart*

> $\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$

$$\sigma := \frac{R\,T}{F^2\,Co\,\sqrt{Do}}$$

> $z0 := r0\,\sqrt{\frac{I\,\omega}{Do}}$

$$z0 := r0\,\sqrt{\frac{\mathrm{I}\,\omega}{Do}}$$

> $Zw := \frac{\sigma\,\mathrm{BesselK}(0, z0)}{\sqrt{I\,\omega}\;\mathrm{BesselK}(1, z0)}$

$$Zw := \frac{R\,T\,\mathrm{BesselK}\left(0, r0\,\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}\;\mathrm{BesselK}\left(1, r0\,\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\right)}$$

> $Zf := Rct + Zw$

$$Zf := Rct + \frac{R\,T\,\mathrm{BesselK}\left(0, r0\,\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\right)}{F^2\,Co\,\sqrt{Do}\,\sqrt{\mathrm{I}\,\omega}\;\mathrm{BesselK}\left(1, r0\,\sqrt{\frac{\mathrm{I}\,\omega}{Do}}\right)}$$

> $Z := Rs + \frac{1}{\frac{1}{Zf} + I\,\omega\,Cdl}$

> $ZM := \sqrt{Z1^2 + Z2^2}$

$$ZM := \sqrt{Z1^2 + Z2^2}$$

> $Z1 := \Re(Z)$

> $Z2 := \Im(Z)$

> $\omega := 10^{lom}$

$$\omega := 10^{lom}$$

> $Rs := 10$

$$Rs := 10$$

> $Cdl := 0.000020$

$$Cdl := 0.000020$$

> $Do := 0.00001$

$$Do := 0.00001$$

> $F := 96485$

$$F := 96485$$

> $T := 298$

$$T := 298$$

> $R := 8.31447$

$$R := 8.31447$$

> $Rct := 50$

$$Rct := 50$$

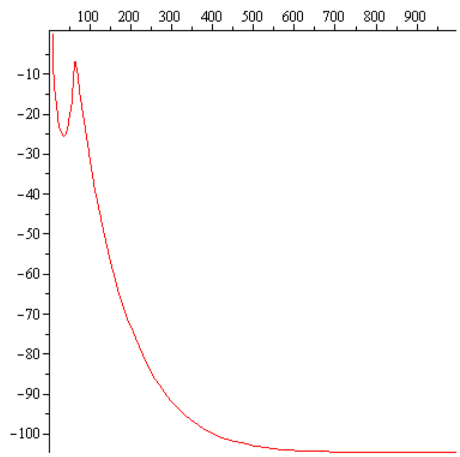
> $Co := 0.000002$

$$Co := 0.000002$$

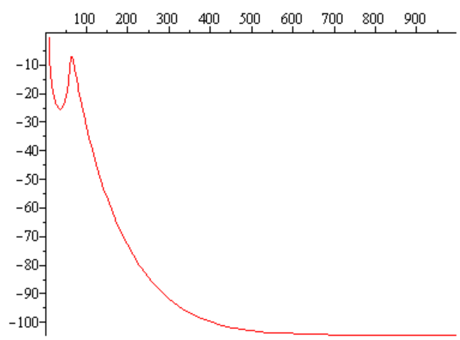
> $r0 := 0.01$

$$r0 := 0.01$$

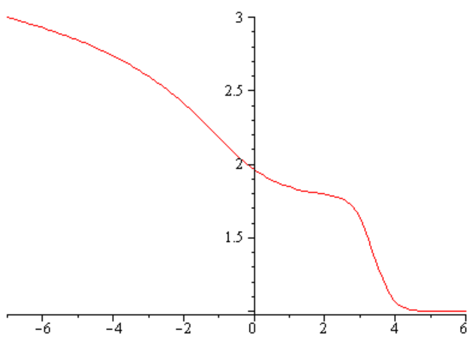
> $plot([Z1, Z2, lom = -7..6])$



> $plot([Z1, Z2, lom = -7..6])$

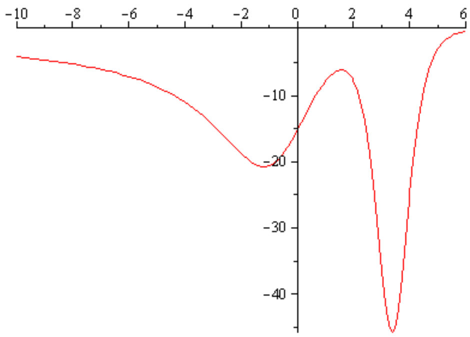


> $plot([lom, \log10(ZM), lom = -7..6])$



$$> \phi := \frac{\arctan\left(\frac{Z2}{Z1}\right) \cdot 180}{\pi}$$

$$> plot([lom, \phi, lom = -10..6])$$



> *filenamebase* := "cyl-Maple

filenamebase := "cyl-Maple

> *filename* := *cat*(*currentdir*( ), "\\", *filenamebase*, ".txt") :
>

```
dat := NULL :
for lom from -4 to 6 by 0.1 do
dat := dat, [lom, Z1(lom), Z2(lom)];
end do:
dat := evalf([dat]) :
```

> *writedata*(*filename*, *dat*, *float*)

Exercise 4.8.

Write a Maple/Mathematica program to calculate Φ_4 and Φ_5 for diffusion to disk electrode.

The results are in 4-8.mw and 4-8.nb.

Definition: a2 = r0^2*omega/D. Example is shown for the parameter a2 = 9 but it can be modified for other values.

> *restart*

$$> a2 = \frac{r0^2\,\omega}{\mathrm{D}}$$

$$a2 = \frac{r0^2\,\omega}{\mathrm{D}}$$

$$> a2 := 9$$

$$a2 := 9$$

$$> a := \sqrt{a2}$$

$$a := 3$$

$$> P4 := \frac{\mathrm{BesselJ}(1, x\,a)^2 \cos\left(\frac{\arctan\left(\frac{1}{x^2}\right)}{2}\right)}{x\,(1+x^4)^{\frac{1}{4}}}$$

$$P4 := \frac{\mathrm{BesselJ}(1, 3\,x)^2 \cos\left(\frac{1}{2}\arctan\left(\frac{1}{x^2}\right)\right)}{x\,(1+x^4)^{1/4}}$$

> $\Phi 4 := \int_0^{\infty} P4 \, dx$

$$\Phi 4 := \int_0^{\infty} \frac{\mathrm{BesselJ}(1, 3\,x)^2 \cos\left(\frac{1}{2} \arctan\left(\frac{1}{x^2}\right)\right)}{x\,(1+x^4)^{1/4}} \, dx$$

> $evalf(\Phi 4)$

$$0.3506383257$$

> $P5 := \frac{\mathrm{BesselJ}(1, x\,a)^2 \sin\left(\frac{\arctan\left(\frac{1}{x^2}\right)}{2}\right)}{x\,(1+x^4)^{\frac{1}{4}}}$

$$P5 := \frac{\mathrm{BesselJ}(1, 3\,x)^2 \sin\left(\frac{1}{2} \arctan\left(\frac{1}{x^2}\right)\right)}{x\,(1+x^4)^{1/4}}$$

> $\Phi 5 := \int_0^{\infty} P5 \, dx$

$$\Phi 5 := \int_0^{\infty} \frac{\mathrm{BesselJ}(1, 3\,x)^2 \sin\left(\frac{1}{2} \arctan\left(\frac{1}{x^2}\right)\right)}{x\,(1+x^4)^{1/4}} \, dx$$

> $evalf(\Phi 5)$

$$0.2464288469$$

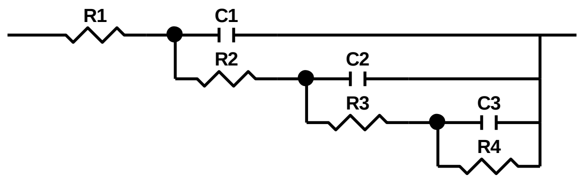
Note, that the integration procedure converges in Maple 13 but not in Maple 6.

Compare with the results in: Ultramicroelectrodes, Ed. by M. Fleischmann, S. Pons, D.R. Rolison and P.P. Schmidt, Datatech Systems, Inc., Morganton, NC, 1987, Chap. 2, p. 57.

Exercise 5.1.

Simulate in ZView plots in Fig. 5.6 (book).

First, prepare the corresponding circuit in Fig. 5.5. The corresponding file is 5-1.mdl.

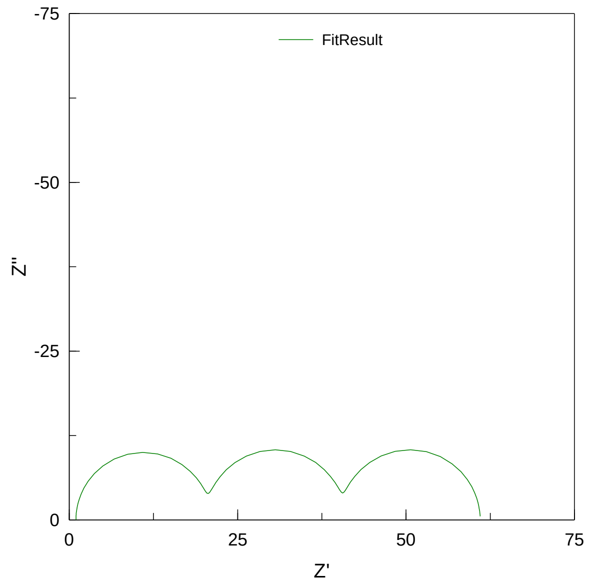


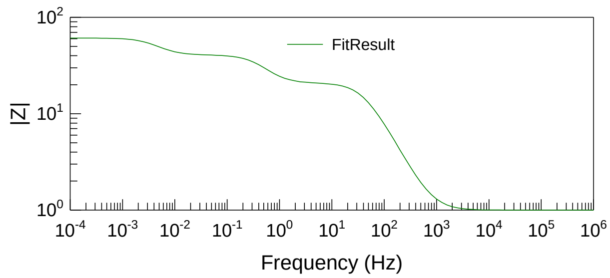
Element	Freedom	Value	Error	Error %
R1	Fixed(X)	1	N/A	N/A
C1	Fixed(X)	0.0002	N/A	N/A
R2	Fixed(X)	20	N/A	N/A
C2	Fixed(X)	0.02	N/A	N/A
R3	Fixed(X)	20	N/A	N/A
C3	Fixed(X)	2	N/A	N/A
R4	Fixed(X)	20	N/A	N/A

Fig. 5.1. Circuit in ZView for

Exercise 5.1.

Next, substitute the corresponding values and run the simulation. For the above data the following graphs are obtained:





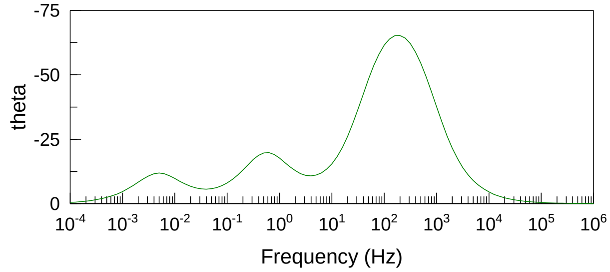


Fig. 5.2. Results of the simulations for the first set of parameters.

Continue simulations for the other sets of data.

Exercise 9.1.

Using Maple or Mathematica simulate impedance described by Eq. (9.18) using data from Fig. 9.15 (book).

The solution can be found in files 9-1.msw and 9-1.nb.

> *Z pore, IPE, Bisquert*

Z pore, IPE, Bisquert

> *restart*

> $\lambda := \sqrt{\frac{z}{re + rs}}$

$$\lambda := \sqrt{\frac{z}{re + rs}}$$

> $z := \frac{1}{I\,\omega\,cdl}$

$$z := -\frac{\mathrm{I}}{\omega\,cdl}$$

> $Rop := \frac{(re^2 + rs^2)\,l}{re + rs}$

$$Rop := \frac{(re^2 + rs^2)\,l}{re + rs}$$

> $Rop1 := \frac{re\,rs\,l}{re + rs}$

$$Rop1 := \frac{re\,rs\,l}{re + rs}$$

> $\Lambda := \frac{l}{\lambda}$

$$\Lambda := \frac{l}{\sqrt{-\frac{\mathrm{I}}{\omega\,cdl\,(re + rs)}}}$$

> $A1 := Rop1\left(1 + \frac{2}{\Lambda\,\sinh(\Lambda)}\right)$

$$A1 := \frac{re\,rs\,l\left(1 + \frac{2\sqrt{-\frac{\mathrm{I}}{\omega\,cdl\,(re + rs)}}}{l\,\sinh\left(\frac{l}{\sqrt{-\frac{\mathrm{I}}{\omega\,cdl\,(re + rs)}}}\right)}\right)}{re + rs}$$

> $A2 := \frac{Rop\,\coth(\Lambda)}{\Lambda}$

$$A2 := \frac{1}{re + rs}\left(\left(re^2 + rs^2\right) \coth\left(\frac{l}{\sqrt{-\frac{I}{\omega\, cdl\, (re + rs)}}}\right)\sqrt{-\frac{I}{\omega\, cdl\, (re + rs)}}\right)$$

> $Z := A1 + A2 :$

> $re := 200$

$$re := 200$$

> $rs := 50$

$$rs := 50$$

> $l := 0.05$

$$l := 0.05$$

> $cdl := 0.001$

$$cdl := 0.001$$

> Rop

$$8.500000000$$

> $Rop1$

$$2.000000000$$

> $Z1 := \Re(Z) :$

> $Z2 := \Im(Z) :$

> $ZA11 := \Re(A1) :$

> $ZA12 := \Im(A1) :$

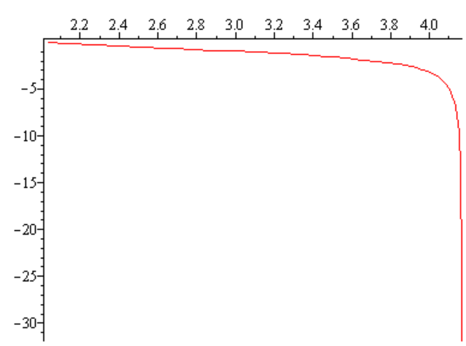
> $ZA21 := \Re(A2) :$

> $ZA22 := \Im(A2) :$

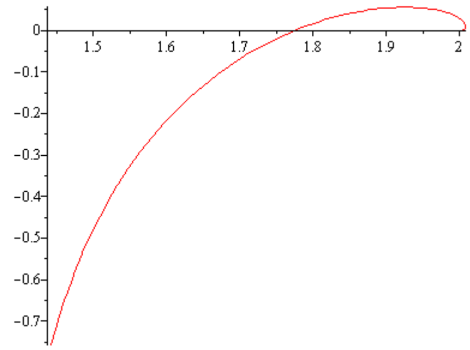
> $\omega := 10^{lof} \cdot 2\, evalf(\pi)$

$$\omega := 6.283185308\; 10^{lof}$$

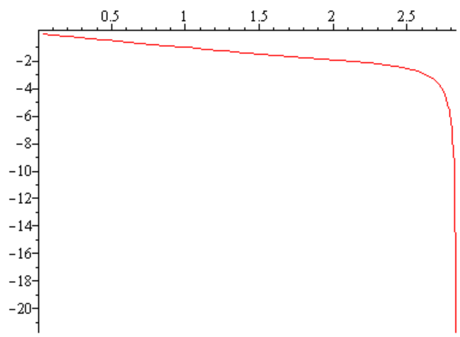
> $plot([Z1, Z2, lof = 2 ..7])$



> $plot([ZA11, ZA12, lof = 3 ..7])$



> *plot*([*ZA21*, *ZA22*, *lof* = 2 ..7])




```
> filenamebase := "pores1-Maple'
                    filenamebase := "pores1-Maple'
> filename := cat(currentdir( ), "\\", filenamebase, ".txt") :
>
   dat := NULL :
   for lof from −2 to 6 by 0.1 do
   dat := dat, [lof, Z1(lom), Z2(lom)]
   end do:
   dat := evalf([dat]) :

> writedata(filename, dat, float)
```

Exercise 9.2.

Simulate impedances defined in Eq. (9.16) using ZView and then approximate them using de Levi's classical model. This model might be found in the new version of ZView only. Use the following parameters: r_e = 200 Ω cm^{-1}, r_s = 50 Ω cm^{-1}, c_{dl} = 0.001 F cm^{-1}, l = 0.05 cm.

Eq. (8.18) is used in ZView in distributed elements: DX Type 1 – Electrochemistry in Macrohomogeneous Porous Electrodes, element Paasch #1. In the description of this element it is stated that the original equation is rearranged into a slightly different form:

$$Z(\omega) = X_A\left[\frac{\coth(B)}{B}\right] + X_B\left[1 + \frac{2}{\sinh(B)}\right] \tag{9.1}$$

where:

$$X_A = R_{\Omega,\mathrm{p}},\ X_B = \bar{R}_{\Omega,\mathrm{p}},\ B = \Lambda^{1/2},\ \text{and}\ \ B = \sqrt{\frac{k + j\omega}{\omega_1}} \tag{9.2}$$

In the expression for B, k = 0 and $\omega_1 = 1/[l^2 c_{\mathrm{dl}}(r_s + r_e)]$. Substituting the values of parameters one should use the following model in Fig. 9.1-9.2 and run the simulation for the frequency range 0.01 to 10^7 Hz. Note that DX-T=ω_1, DX-A=X_A, and DX-B=X_B. Then save the obtained data file (9-2.z) and make approximation using the model consisting of the solution resistance R1 and de Levie element: Ls - de Levie Pore – Finite Length in series. Open the saved file and run fitting, all points, Calc-Modulus weighting. The obtained parameters are displayed in Fig. 9.2. The data obtained consisting of three columns: frequency, Z', and Z" were approximated by the model consisting of the solution resistance, R_1 in series with the de Levie's porous electrode element Ls.

Element	Freedom	Value	Error	Error %
DX1	Fixed(X)	1: Paasch #1		
DX1-R	Fixed(X)	0	N/A	N/A
DX1-T	Fixed(X)	1600	N/A	N/A
DX1-P	Fixed(X)	0	N/A	N/A
DX1-U	Fixed(X)	0	N/A	N/A
DX1-A	Fixed(X)	8.5	N/A	N/A
DX1-B	Fixed(X)	2	N/A	N/A

Fig. 9.1. Electrical equivalent model used for simulation of the model described by Eq. (9.1).

Element	Freedom	Value	Error	Error %
R1	Free(+)	1.99	0.0033054	0.1661
Ls1-A	Fixed(X)	1E20	N/A	N/A
Ls1-B	Free(+)	0.00030335	1.9373E-06	0.63864
Ls1-Phi	Fixed(X)	1	N/A	N/A
Ls1-R	Free(+)	6.076	0.037451	0.61638

Chi-Squared: 0.0041137
Weighted Sum of Squares: 0.81863

Fig. 9.2. Results of the approximation of the impedances simulated using model in Fig. 9.1 by the model consisting of solution resistance in series with the de Levie's porous model.

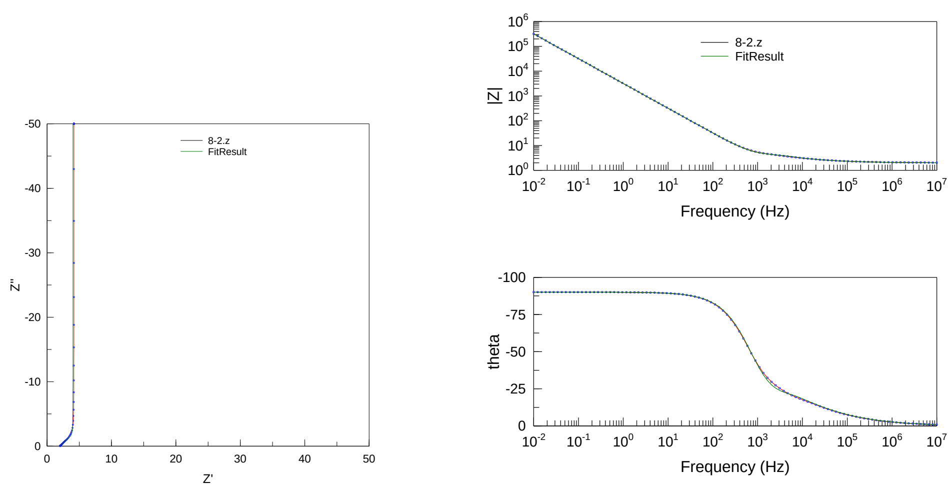


Fig. 9.3. Complex plane and Bode plots of data simulated using Paasch #1 model, Eq. (9.1) and fitted to the de Levies porous model.

It is defined as:

$$Z = \left(\frac{R}{\Lambda^{1/2}}\right)\coth\left(\Lambda^{1/2}\right) \tag{9.3}$$

where

$$\Lambda = \frac{1}{A} + B(j\omega)^{\phi} \tag{9.4}$$

The parameter A corresponding to the kinetics was fixed as very large, 10^{20}, therefore $1/A = 10^{-20}$ that is negligible. The constant phase exponent $\phi = 1$ because the system is purely capacitive at low frequencies. The standard deviations of the obtained parameters are small which confirms that the fit is good. Assuming $r_s = 0$, Eq. (9.18), book, reduces to the de Levie's equation:

$$Z = (r_e l)\frac{\coth\left(\sqrt{j\omega l^2 c_{dl} r_s}\right)}{\sqrt{j\omega l^2 c_{dl} r_s}} = R_{\Omega,p}\frac{\coth\left(\Lambda^{1/2}\right)}{\Lambda^{1/2}} \tag{9.5}$$

The ZView models are in files 9-2-Paasch1.mdl and 9-2-deLevie.mdl while the simulated data are in 9-2.z, book.

Exercise 9.3.

Using Maple or Mathematica simulate impedance described by Eq. (9.16) and (9.30) using data from Fig. 9.20 (book).

The program is in file 9-3.mw and 9-3.nb.

> *restart*

> $\lambda := \sqrt{\frac{z}{re + rs}}$

$$\lambda := \sqrt{\frac{z}{re + rs}}$$

> $z := \frac{1}{\frac{1}{rct} + I\,\omega\,cdl}$

$$z := \frac{1}{\frac{1}{rct} + \mathrm{I}\,\omega\,cdl}$$

> $Rop := \frac{(re^2 + rs^2)\,l}{re + rs}$

$$Rop := \frac{(re^2 + rs^2)\,l}{re + rs}$$

> $Rop1 := \frac{re\,rs\,l}{re + rs}$

$$Rop1 := \frac{re\,rs\,l}{re + rs}$$

> $\Lambda := \frac{l}{\lambda}$

$$\Lambda := \frac{l}{\sqrt{\frac{1}{\left(\frac{1}{rct} + \mathrm{I}\,\omega\, cdl\right)(re + rs)}}}$$

$> A1 := Rop1 \left(1 + \frac{2}{\Lambda \sinh(\Lambda)}\right)$

$> A2 := \frac{Rop \coth(\Lambda)}{\Lambda}$

$> Z := A1 + A2 :$

$> re := 200$

$$re := 200$$

$> rs := 50$

$$rs := 50$$

$> l := 0.05$

$$l := 0.05$$

$> cdl := 0.001$

$$cdl := 0.001$$

$> rct := 1$

$$rct := 1$$

$> Rop$

$$8.500000000$$

$> Rop1$

$$2.000000000$$

$> Z1 := \Re(Z) :$

$> Z2 := \Im(Z) :$

$> ZA11 := \Re(A1) :$

$> ZA12 := \Im(A1) :$

$> ZA21 := \Re(A2) :$

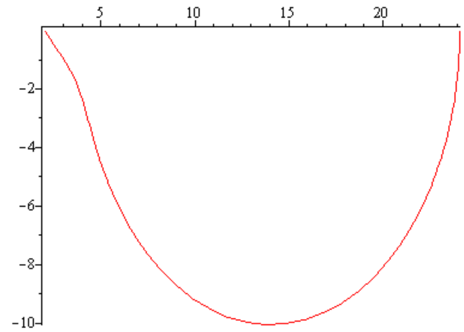
$> ZA22 := \Im(A2)$

$$ZA22 := \frac{17}{25} \sqrt{250}\, \Im\left(\coth\left(\frac{0.05 \sqrt{250}}{\sqrt{\frac{1}{1 + 0.001\,\mathrm{I}\,\omega}}}\right) \sqrt{\frac{1}{1 + 0.001\,\mathrm{I}\,\omega}}\right)$$

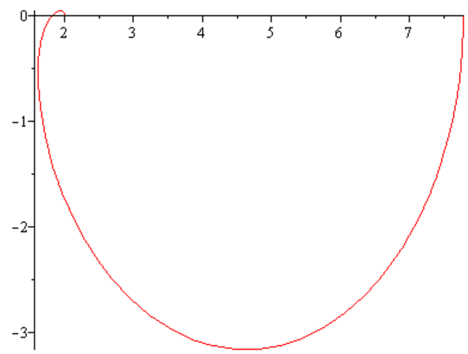
$> \omega := 10^{lof} \cdot 2\, evalf(\pi)$

$$\omega := 6.283185308\ 10^{lof}$$

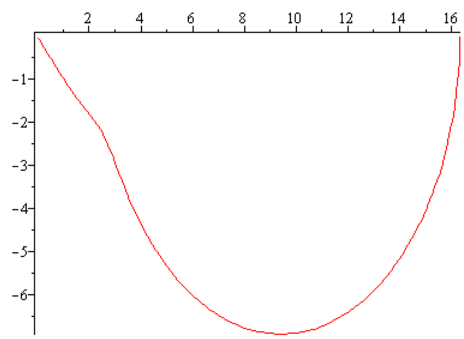
$> plot([Z1, Z2, lof = -2..7])$



> *plot*([*ZA11*, *ZA12*, *lof* = −2 ..7])



> *plot*([*ZA21*, *ZA22*, *lof* = −2 ..7])



> *filenamebase* := "pores2-Maple"

filenamebase := "pores2-Maple"

> *filename* := *cat*(*currentdir*( ), "\\", *filenamebase*, ".txt") :

```
>
 dat := NULL :
 for lof from −2 to 6 by 0.1 do
 dat := dat, [lof, Z1(lom), Z2(lom)]
 end do:
 dat := evalf([dat]) :
```

> *writedata*(*filename*, *dat*, *float*)

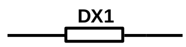
Exercise 9.4.

Simulate impedance of the porous electrode in the presence of the solution and electrode resistance and red-ox system using ZView. Use parameters from Fig. 9.20. Fit the obtained data to the simple de Levie’s model.

To simulate Eq. (9.18) in ZView the distributed elements: DX Type 1 – Electrochemistry in Macrohomogeneous Porous Electrodes should be used. Comparison of Eqs. (9.2)-(9.3) and (9.17)-(9.17) book, shows that the parameter k = DX-R is:

$$k = \frac{1}{r_{\mathrm{ct}} c_{\mathrm{dl}}} = 1000\ \mathrm{s}^{-1} \tag{9.6}$$

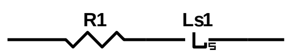
and all other parameters are the same as in Exercise 9.2. The input parameters are displayed in Fig. 9.4.



Element	Freedom	Value	Error	Error %
DX1	Fixed(X)	1: Paasch #1		
DX1-R	Fixed(X)	1000	N/A	N/A
DX1-T	Fixed(X)	1600	N/A	N/A
DX1-P	Fixed(X)	0	N/A	N/A
DX1-U	Fixed(X)	0	N/A	N/A
DX1-A	Fixed(X)	8.5	N/A	N/A
DX1-B	Fixed(X)	2	N/A	N/A

Fig. 9.4. Input parameters in simulation of impedances in ZView using model DX1, Eq. (8.18).

Next, the results must be saved in data file with extension "z" and approximated using de Levie's model R1 – Ls1. The obtained results are shown in Fig. 9.5.



Element	Freedom	Value	Error	Error %
R1	Free(+)	1.993	0.0025315	0.12702
Ls1-A	Free(+)	3.447	0.022585	0.65521
Ls1-B	Free(+)	0.00028447	2.3563E-06	0.82831
Ls1-Phi	Fixed(X)	1	N/A	N/A
Ls1-R	Free(+)	5.852	0.035264	0.6026

Chi-Squared: 0.0012176
Weighted Sum of Squares: 0.24108

Fig. 9.5. Results of the approximation of the impedances simulated using model in Fig. 9.4 by the de Levie's porous electrode model.

The ZView models are in files 9-4-Paasch1.mdl and 9-4-deLevie.mdl while the simulated data are in 9-4.z.

Visual comparison of the complex plane and Bode plots shows that the approximation is good with the standard deviation of parameters of ≤0.8%. However, when $r_{\mathrm{e}} = r_{\mathrm{s}} = 200\ \Omega\ \mathrm{cm}^{-1}$ the approximations are ideal.

The results obtained above show again that without a priori knowledge of the solution and electrode resistivities the full equation Eq. (8.18) cannot be used because the system might be well approximated by a simpler model involving solution resistance only, Eq. (8.7).

Exercise 13.1.

Carry out K-K transform of the data in the file 1.z.

Kramers-Kronig transformations in this chapter are carried out using Boukamp's program KKtest.exe available for download on the Internet at: http://www.utwente.nl/tnw/ims/publication/downloads/ as a zipped file: KK-windows.zip. The theory is described in the corresponding paper.[4] It is sufficient to copy data to the folder containing KKtest.exe file. There is also a manual: Kramers-Kronig Manual.pdf.

The program reads a simple file containing three columns: frequency, Z' and Z". It can perform impedance or admittance transform selectable from KK-Transform, Transform Setting menu. The program allows also for saving the original and transformed data in a data file.

After execution of the file the data should be read into the program. They are immediately displayed, see Fig. 13.1. Next, choose KK-Transform and Transform settings. Choose Transform Mode: Impedance. The obtained image is also displayed in Fig. 13.1.

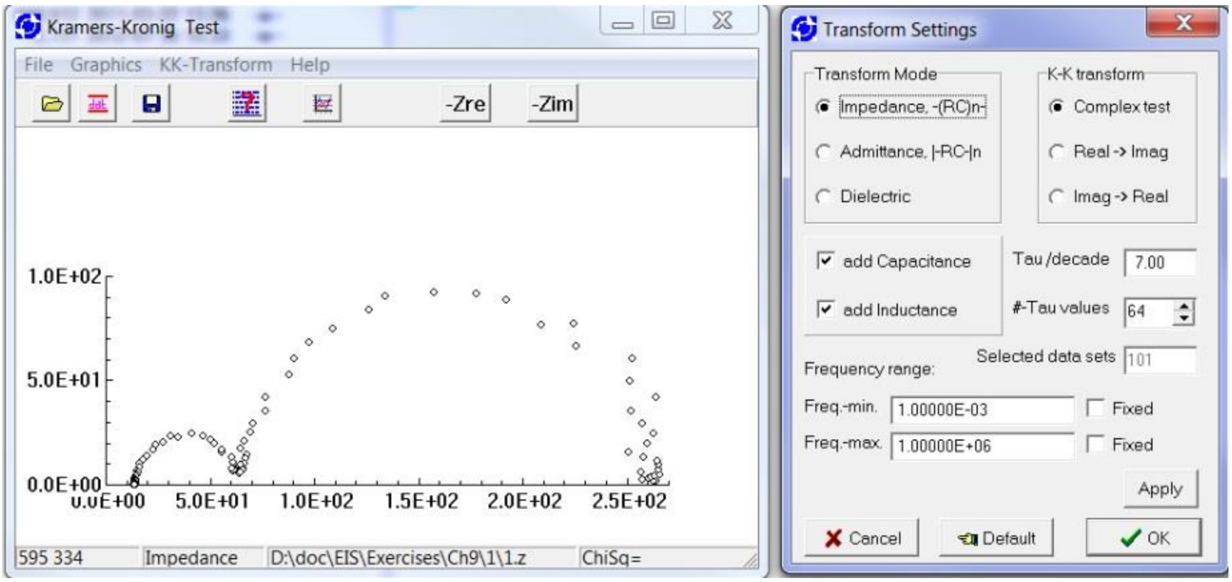


Fig. 13.1. Windows obtained during execution of KKtest.exe, after reading data: 1.z and choosing Transform Settings from KK-transform.

Next, select Do KK-transform from KK-Transform. The relative errors between the experimental and transformed impedances are displayed as in Fig. 13.2. It is evident that the relative errors are distributed randomly around zero line and complex plane plots are similar without any systematic deviations.

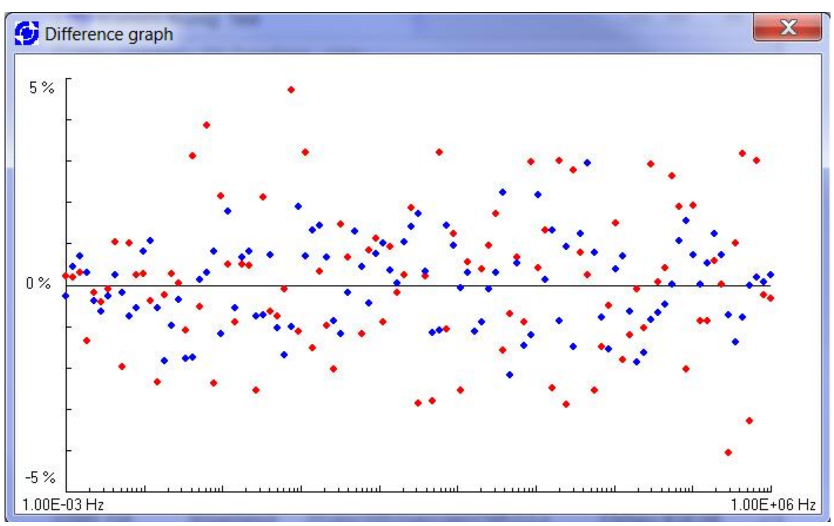


Fig. 13.2. Relative errors of the real and imaginary experimental and KK transformed impedances for file 1.z.

After closing this window comparison of the complex plane plots of the experimental and transformed impedances is displayed, Fig. 13.3. It is evident that the errors are random as there are no systematic deviations. One may conclude that this data passed KK test.

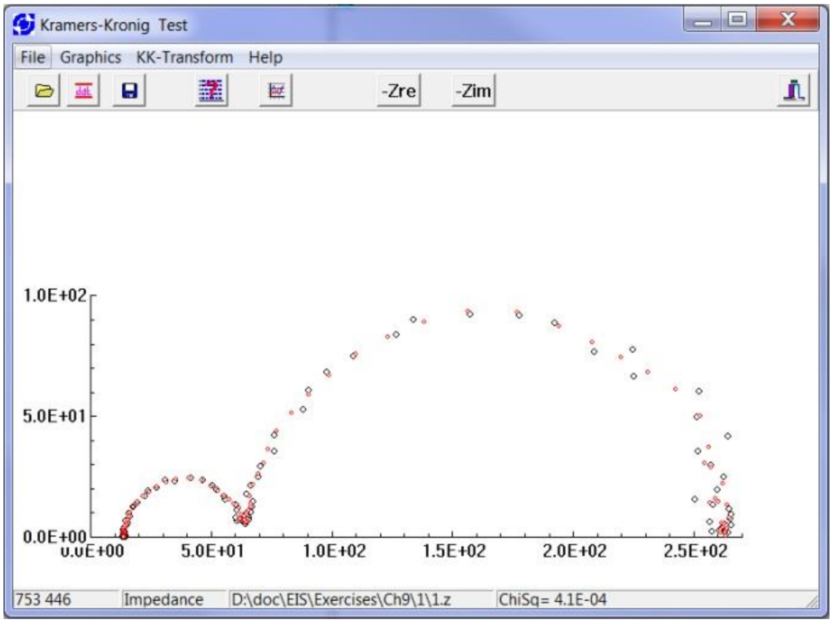


Fig. 13.3. Comparison of the experimental and transformed complex plane plots.

The above KK test was carried out on impedances. One can also choose Transform Mode: Admittances from Transform Settings. This performs KK transform admittances but displays the results as impedances. Running such a test for the above data gives the same relative errors and impedances. This indicates that for the above data (which contains positive resistances and capacitances) these two tests are equivalent.

Exercise 13.2.

Carry out K-K transform of the data in the file 2.z.

The results of the KK test shows are displayed in Fig. 13.4 and 13.5.

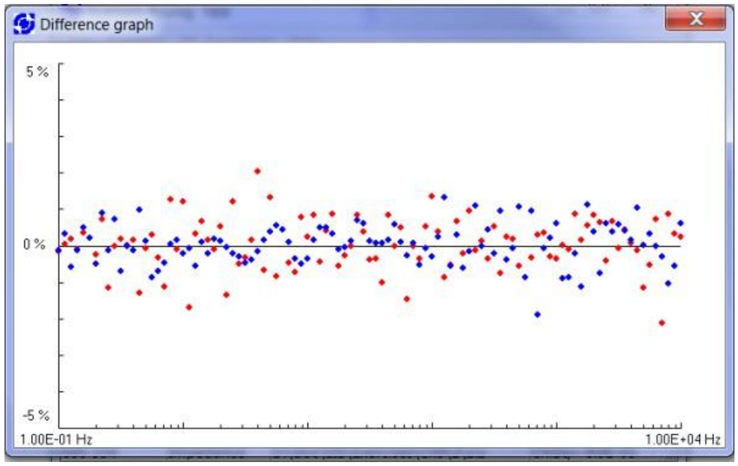


Fig. 13.4. Relative errors of the real and imaginary experimental and KK transformed impedances for file 2.z.

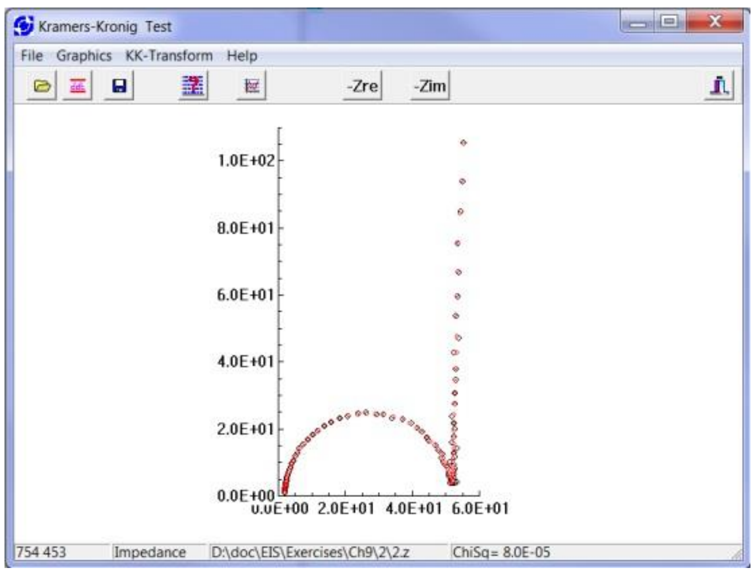


Fig. 13.5. Comparison of the experimental and KK transformed impedances for file 2.z.

It is obvious that the differences between the experimental and KK transformed impedances are random and the complex plane plots agree well. This means that the data are KK transformable.

Exercise 13.3.

Carry out K-K transform of the data in the file 3.z.

The results of the KK test of impedances shows are displayed in Fig. 13.6 and 13.7.

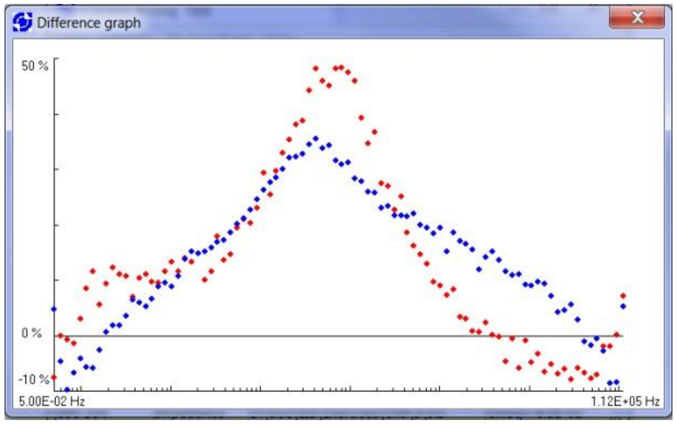


Fig. 13.6. Relative errors of the real and imaginary experimental and KK transformed impedances for file 3.z.

In this case very large (up to 50%) systematic (not random) differences between the experimental and transformed data are found and the complex plane plots are also different. The same errors appear when the admittances are transformed. These data are not KK transformable therefore cannot be used in further analysis.

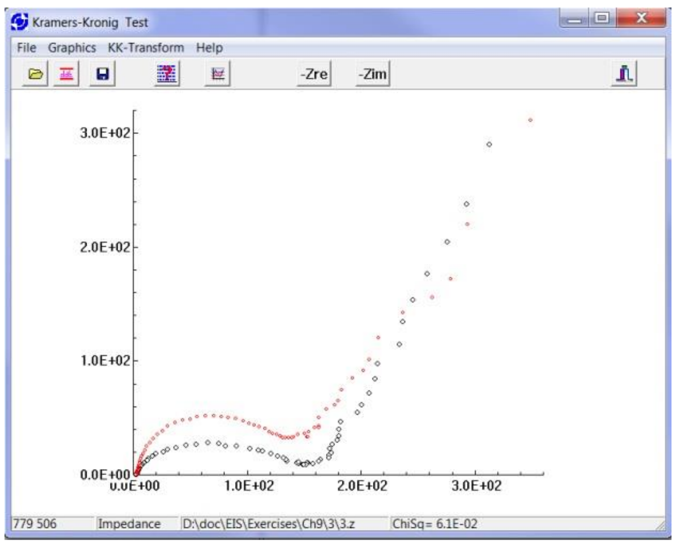


Fig. 13.7. Comparison of the experimental and KK transformed impedances for file 3.z.

Exercise 13.4.

Perform K-K transform of the data in the file 4.z.

The results of the KK test performed in the impedance mode are displayed in Fig. 13.8 and 13.9.

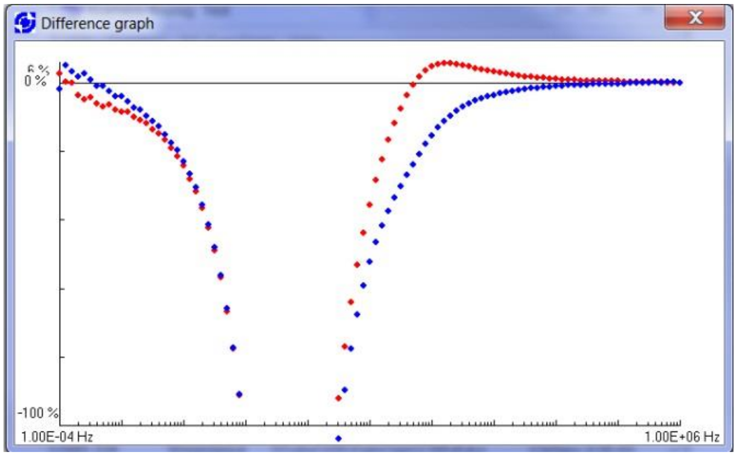


Fig. 13.8. Relative errors of the experimental real and imaginary impedances and KK transformed impedances for file 4.z. KK test performed on impedances.

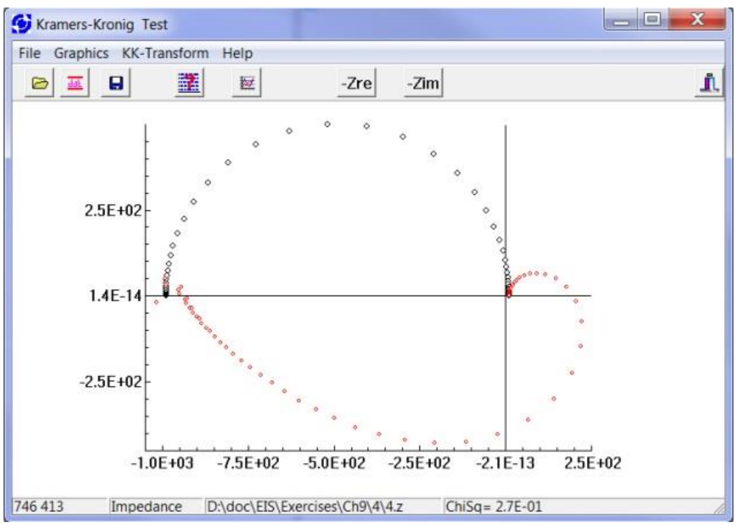


Fig. 13.9. Comparison of the experimental and KK transformed impedances for file 4.z. KK test performed on impedances.

It is evident than the relative errors and the complex plane plots of the experimental and transformed impedances show systematic differences and are completely different. However, form Fig. 13.9 it is visible that the low frequency resistance is negative (and the capacitance positive because the imaginary impedances are always negative). In such a case the KK transform should be carried out on admittances. Therefore, the Admittance Mode should be selected and the KK transformation performed on admittances. The results of such test are shown in Fig. 13.10 and 13.11.

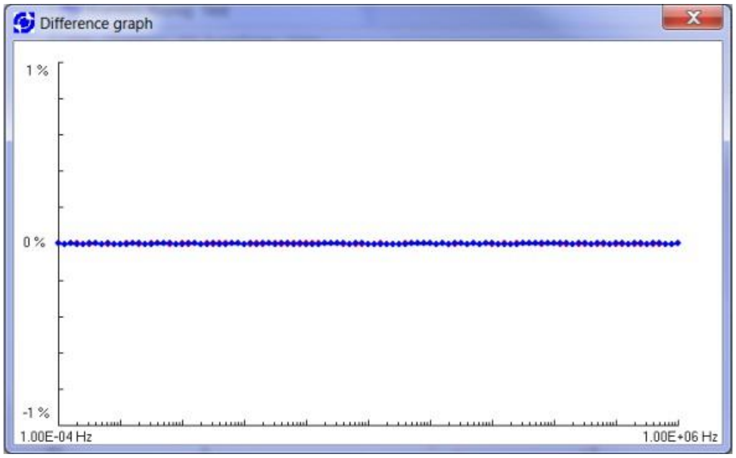


Fig. 13.10. Relative errors of the experimental real and imaginary impedances and KK transformed impedances for file 4.z. KK test performed on admittances.

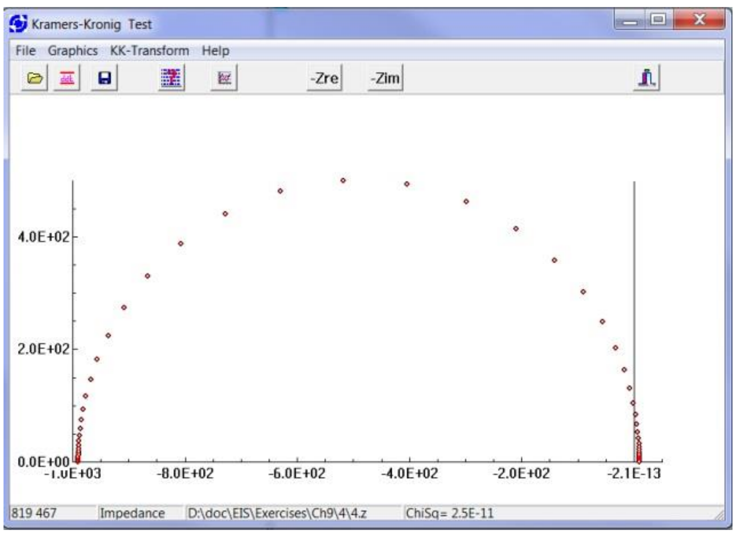


Fig. 13.11. Comparison of the experimental and KK transformed impedances for file 4.z. KK test performed on admittances.

The above analysis shows that in the case of the negative charge transfer resistance the KK test fails for impedances but passes for admittances, in agreement with the theory.

Exercise 13.5.

Perform K-K transform of the data in the file 5.z.

The results of the KK test performed in the impedance mode are displayed in Fig. 13.12 and 13.13.

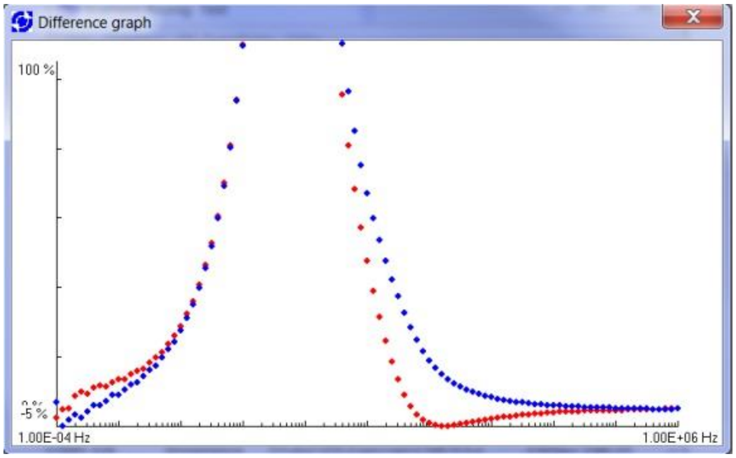


Fig. 13.12. Relative errors of the experimental real and imaginary impedances and KK transformed impedances for file 5.z. KK test performed on impedances.

The results of the KK test carried out on impedances show large systematic differences between the experimental and transformed data.

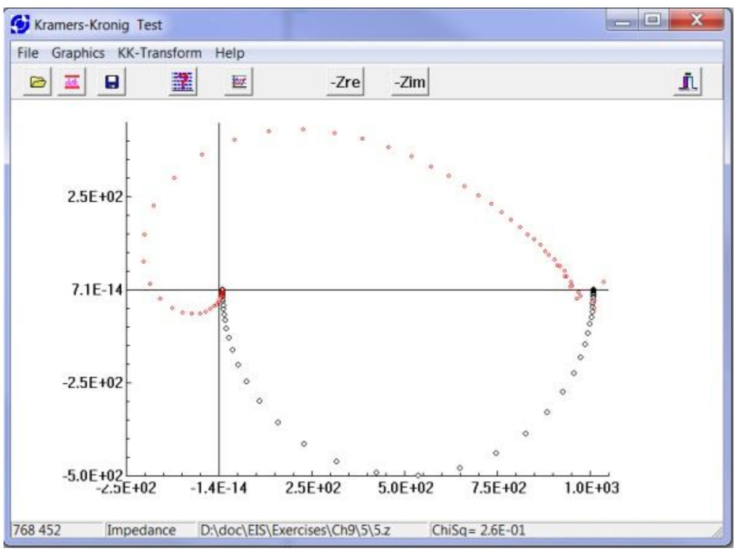


Fig. 13.13. Comparison of the experimental and KK transformed impedances for file 5.z. KK test performed on impedances.

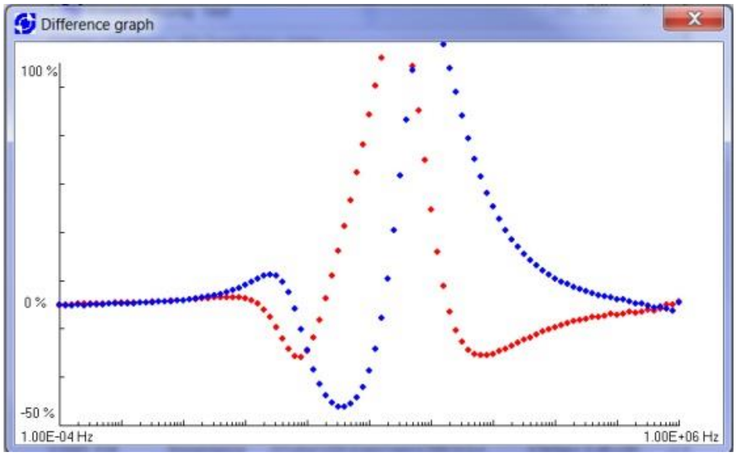


Fig. 13.14. Relative errors of the experimental real and imaginary impedances and KK transformed impedances for file 5.z. KK test performed on admittances.

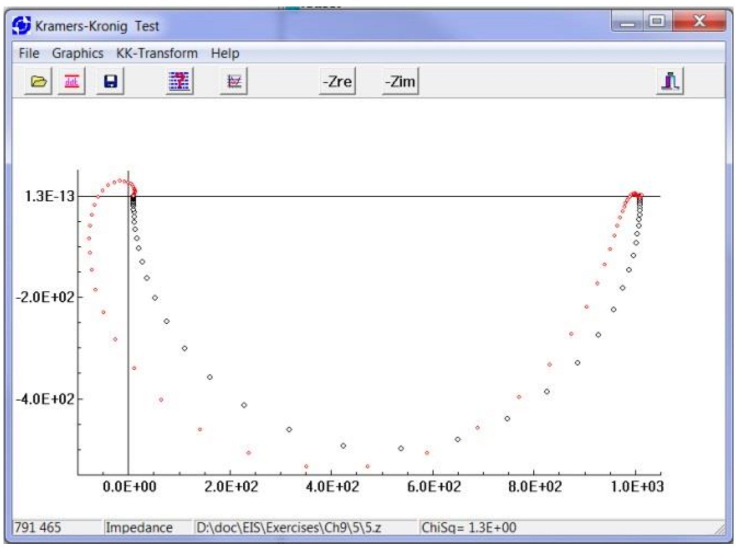


Fig. 13.15. Comparison of the experimental and KK transformed impedances for file 5.z. KK test performed on admittances.

Because the impedance test failed it was also carried out on admittances; the results are shown in Fig. 13.14 and 13.15. As before there are large systematic differences between the experimental and KK transformed data. This means that the data are not KK transformable. In fact, one can notice that the data correspond to the positive charge transfer resistance and negative capacitance.

Exercise 14.1.

Determine the error structure of the impedance in files Z1.z, Z2.z, Z3.z, and Z4.z using Orazem's measurement model approach and determine the impedance parameters for Z1.z using circuit: $R_s(C_{dl}(R_{ct}Z_{FLW}))$ where Z_{FLW} is the finite length transmissive mass transfer impedance.

First, fit to the Voigt model containing three or more (*RC*) parallel elements: *R*(*RC*)(*RC*)(*RC*)… must be carried out. All the results are displayed in Excel file Ex14-1.xlsx. This has been carried out for Z1.z in the sheet entitled "finding model" using ZView program. Going from three to four (*RC*) elements an improvement of the fit was observed. However, for 5 (*RC*) elements standard deviation of one of the parameters (C3) was 96.6%. The same procedure was repeated for Z2.z and a similar behavior was found but for 5 (*RC*) elements standard deviation of some parameters is much larger than 100% (reaching 575%). Similar modeling can be carried out for other files. The obtained results indicate that measurement model which should be chosen is the one containing *four* (*RC*) elements.

Data analysis is displayed in the Excel sheet "data analysis". Results of the fit of four data files to the measurement model are shown there together with the data calculated for that model and the complex plane and Bode plots. Next, the deviations between the experimental calculated (model) impedances were used to calculate the sum of squares of deviations:

$$S(f_i) = S_i = \sum_{k=1}^{4} [Z'_k(f_i) - Z'_{k,calc}(f_i)]^2 + [Z''_k(f_i) - Z''_{k,calc}(f_i)]^2 \tag{14.1}$$

for each frequency *i*. Then, σ_i was obtained at each frequency:

$$\sigma_i = \sqrt{\frac{S_i}{8-1}} \tag{14.2}$$

for 7 degrees of freedom as 8 differences (four for real and four for imaginary data) were used at each frequency. The obtained values of σ_i as a function of the logarithm of frequency are displayed in Fig. 14.1.

Next, the experimental standard deviations were fitted to the impedance model

$$\sigma'_i = \sigma''_i = \alpha |Z''_i| + \beta |Z'_i - R_s| + \gamma |Z_i|^2 + \delta \tag{14.3}$$

This is a linear regression of the type $y = b_0 + b_1x_1 + b_2x_2 + b_3x_3$ where y are the experimental values of σ_i and x_i are the three columns containing $|Z''|$, $|Z'|$ and $|Z|^2$. However, this model produced quite large standard deviation for the parameter γ, the value of $|t$ statistical$| = |\gamma / s_\gamma| = 0.769$ (see the regression table in the Excel file) while the theoretical value $t(0.05, 97)=1.985$ which means at 95% probability this value must be rejected. Then, a simpler model was used:

$$\sigma'_i = \sigma''_i = \alpha |Z''_i| + \beta |Z'_i - R_s| + \delta \tag{14.4}$$

For this model the values of t statistical of all parameters are larger than $t(0.05,98) = 1.984$. The predicted values of σ_i were used in the weighting for the determination of the model parameters. Fig. 14.1 presents the plot of the real and imaginary impedances as well as the experimental and calculated from the regression model values of the standard deviation. One can notice that at highest and the lowest frequencies the standard deviations are comparable with the imaginary impedances.

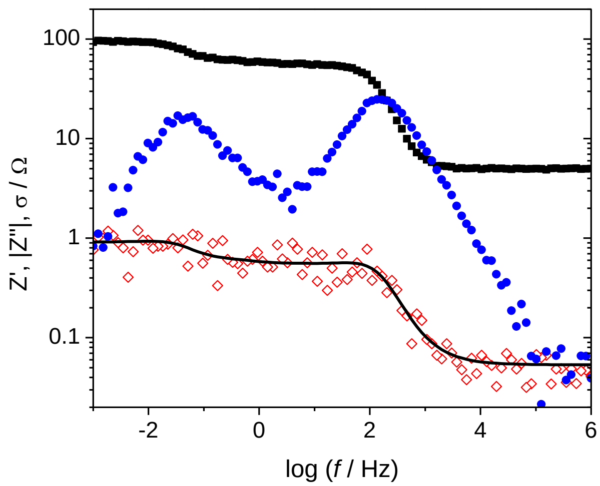


Fig. 14.1. Plot containing real (squares) and imaginary (circles) impedances (from file Z1.z), the experimental values of σ_i (open diamonds) and the values of σ_i calculated from regression simpler model (continuous line).

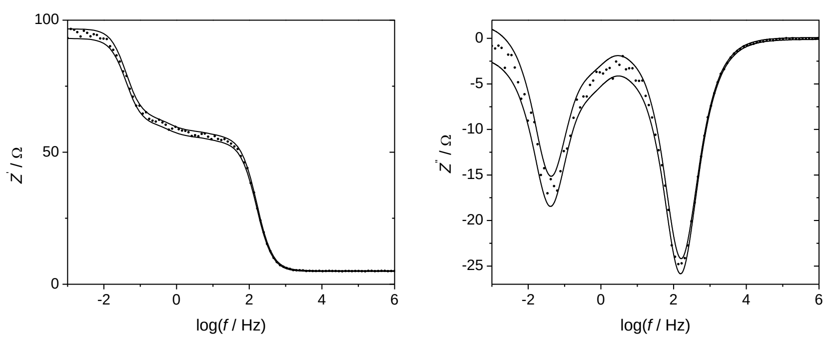


Fig. 14.2. Real and imaginary impedances for Z1.z together with the confidence intervals calculated using σ_i values from regression and 95% probability.

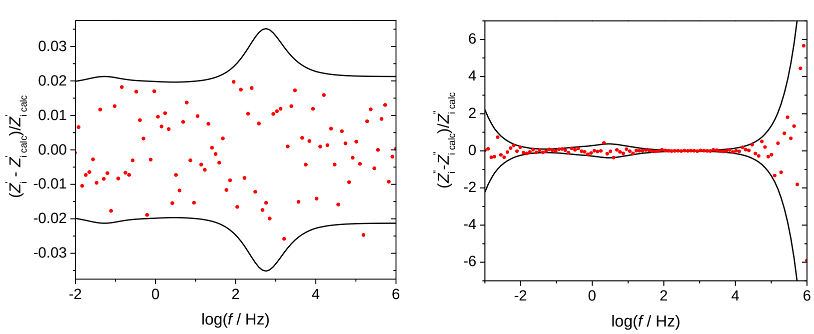


Fig. 14.3. Relative errors of the real and imaginary impedances (circles) for the data in Z1.z and the calculated relative confidence intervals for these impedances for 95% probability.

Fig. 14.2 and 14.3 display impedances and relative errors for the real and imaginary impedances for the data in Z1.z. As continuous lines there are confidence and relative confidence intervals: $Z_i \pm \sigma_i t$ and $\pm\sigma_i t/Z_{i,calc}$, respectively, using $t(0.05,98)$ for 95% probability and 101 points – 3 parameters = 98 degrees of freedom. This means that there is only 5% chance that the experimental data are found outside this interval. In our case all the experimental data are inside these limits.

Finally, having determined the error structure, one should proceed with the determination of the physicochemical model parameters. Because ZView does not allow using external standard deviations it will be carried out using Macdonald's LEVM program.[1] The data must be prepared in a special format from Z1.z. For the approximations circuit B was used. The distributed element Finite Length Warburg is already preprogrammed as a distributed element DE with the control parameter NELEM = 9. It is defined as:

$$Z_{\mathrm{FLW}} = \frac{R \tanh(j\omega T)^{0.5}}{(j\omega T)^{0.5}} \tag{14.5}$$

and depends on two adjustable parameters R and T while the exponent 0.5 is fixed. The following parameters were used in the fit:

R_s = R1 =	P(1)	free
R_{ct} = R2 =	P(4)	free
C_{dl} = C2 =	P(5)	free
R = RDE2 =	P(11)	free
T = TDE2 =	P(12)	free
PDE2 =	P(14)	fixed
NELM =	NDE2 = 9	fixed

All these parameters are included in the INFL file in folder LEVM. Its structure is described in detail in the manual for the program. In INFL file, after the data, there are standard deviations at each frequency obtained from the regression analysis, with the condition: $\sigma_i' = \sigma_i'' = \sigma_i$. To read external standard deviations the parameter IRCH is set to 0. For convenience the TRAD.EXE program which changes the experimental data into the format used by INFL is also included. As an example file aaa containing number of frequencies and data from Z1.z can be easily transformed into file DATA in the proper format. The data should be attached to the proper top-INFL file. Execution of LEVMWIN.exe produces the following results (which can be easily inspected using LEVMVIEW.EXE graphic program):

Table 14.1. Results of the CNLS fit to the circuit $R_s(C_{dl}(R_{ct}Z_{FLW}))$ using calculated standard deviations with LEVM program.

Parameter	Value	Standard deviation	Relative standard deviation
R_s	4.9885	0.0080	1.6×10^{-3}
R_{ct}	49.942	0.094	1.9×10^{-3}
C_{dl}	21.994×10^{-5}	0.0060×10^{-5}	3.0×10^{-3}
R	39.79	0.22	5.5×10^{-3}
T	9.85	0.17	0.017

However, almost identical results were obtained using calculated modulus weighting (see Excel file: Fit comparison). The complex plane plot obtained using LEVMVIEW.EXE utility program is shown below in Fig. 14.4.

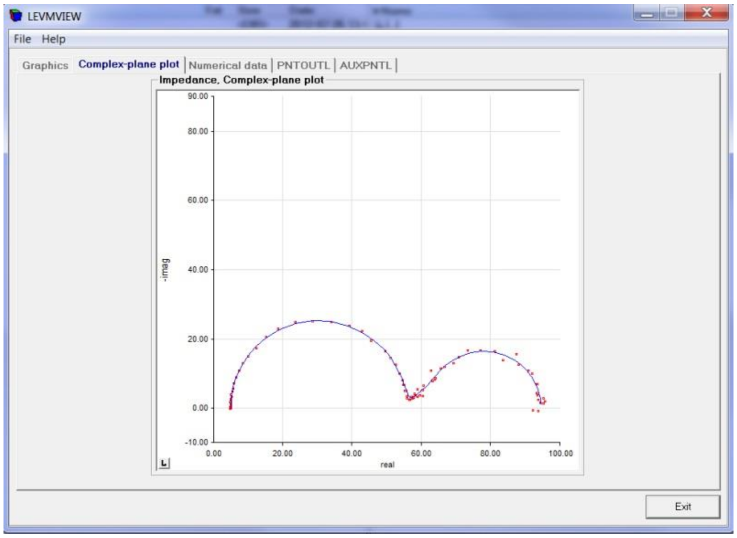


Fig. 14.4. Complex plane plot of the experimental data and approximation using standard deviations from Orazem's measurement model and LEVM program. Plot was obtained using utility LEVMVIEW program.

Exercise 14.2.

Find an electrical equivalent model describing data in file 2.z. Try different weighting techniques. Calculate the sum of squares, S, and reduced sum of squares S_ν. Carry out F-test.

Inspecting the data in ZView shows that the complex plane plot represents a semicircle. The simplest model representing such plot is $R(CR)$. It is created in ZView and saved as $R(CR)$.mdl. The results of approximation, the complex plane and Bode plots are shown Ex14-2.xls. Systematic difference between the experimental data and approximations exist. Moreover, the peak on the Bode phase angle plots is poorly approximated. The approximation results are shown in the following

Table 14.2.

Table 14.2.Results of fit of the data to two models and three weighting models.

Parameter	Model *R*(*CR*)		
	w=1	w=prop	w=modulus
R1	21.06	19.82	20.4
sR1	0.24	0.44	0.1
sR1 %	1.1	2.2	0.43
C1	8.036E-05	7.158E-05	7.538E-05
sC1	7.6E-07	1.3E-07	6.3E-07
sC1%	0.95	1.8	0.84
R2	98.22	112.7	98.27
sR2	0.31	1.3	0.40
sR2 %	0.31	1.2	0.40
S	205.37	1.657	0.0524
Sν	1.57	0.0126	0.00040
Parameter	Model *R*(*QR*)		
	w=1	w=prop	w=modulus
R1	21.01	20.01	19.98
sR1	0.14	0.043	0.04
sR1 %	0.70	0.21	0.18
T1	0.0001011	0.00010030	0.0001015
sT1	0.0000014	0.00000033	0.0000011
sT1%	1.35	0.32	1.1
Phi	0.9482	0.94947	0.9474
sPhi	0.0028	0.00042	0.0018
sPhi%	0.3	0.045	0.20
R2	100.1	99.99	100.2
sR2	0.2	0.14	0.20
sR2 %	0.2	0.14	0.16
S	56.765	0.014127	5.41E-5
Sν	0.6984	0.0001087	0.00102

It should be noticed that the values of S and S_ν for the model modulus weightings calculated in Excel differ from those calculated by ZView. It is related to the fact that the Macdonald's LEVM algorithm is used by ZView in this program for modulus weightings and it is using not directly modulus but calculated uncertainties which are directly proportional to modulus. These details are not explained in the manual. It should be added that these changes do not influence the obtained parameters and their standard deviations.

F-test for the addition of one parameter for modulus weighting (using correct sum of squares calculated in Excel) is $F_{\text{experimental}}$ = (0.05241-0.007083)/(0.007083/(2*67-4) = 832, much larger that the theoretical value of F(0.05, 1, 130) = 3.91 (see Excel file for calculations) and the use of the CPE is statistically justified. The use of the sums of squares from ZView also confirms this statement.

It should also be noticed that in general the relative standard deviations of the parameters decrease when passing to the model containing CPE parameter although even for the inappropriate model containing capacitance the standard deviations are relatively small. Only the *F* test allows to discriminate between two models.

Exercise 14.3.

Fit data 3.z into the nested model $R_s(C_{dl}(R_{ct}(C_pR_p)))$. Check if the use of the CPE elements instead of capacitances is statistically justified.

First, let us build a more general model $R(Q(R(QR)))$; if the parameters CPE-P for both elements Q are $\phi=1$ this model is equivalent to $R(C(R(CR)))$. After reading the experimental data into ZView the initial values of the parameters must be set. As we do not know anything about the capacitances we must choose something, for example as in Fig. 14.5.

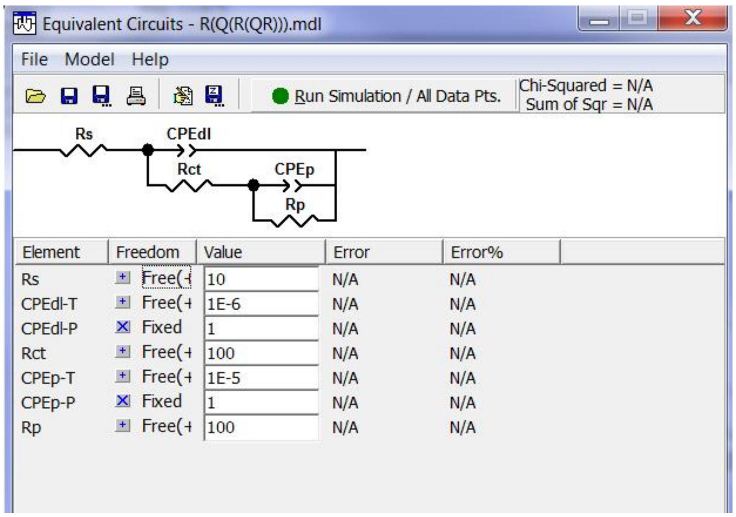
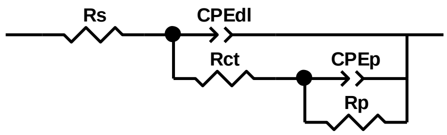


Fig. 14.5. Circuit model $R_s(Q_{dl}(R_{ct}(Q_pR_p)))$ with the initial parameters. After fixing CPEdl-P and CPEp-P to one it is equivalent to $R_s(C_{dl}(R_{ct}(C_pR_p)))$.

Run the fit with calculated modulus weighting; the results obtained are presented in Fig. 14.6. The CNLS program finds the parameters with their standard deviations. All the results are also shown in the Excel file Ex14-3.xlsx.

Next, let us try if the replacement of C_{dl} by the CPE element improves the quality of fit. To do that let us set CPEdl-P as a free parameter and run the fit. The obtained results are displayed in Fig. 14.7. To check if the addition of one free parameter to the model is justified one may use the sequential F-test. To do this we need weighted sum of squares for the simpler fit, $S_1 = 1.3497$ and for the new fit, $S_2 = 0.99331$. The number of the degrees of freedom of the numerator is 1 and that of the denominator is $2\times101-6=196$ as there are 101 frequencies and two impedances (real and imaginary) are determined at each frequency, and there are 6 free parameters in the new fit. The value of F is calculated as follows:

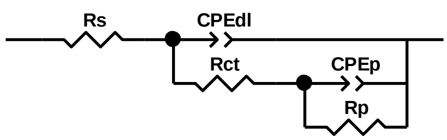


Element	Freedom	Value	Error	Error %
Rs	Free(+)	14.06	0.059095	0.42031
CPEdl-T	Free(+)	9.2617E-06	1.0222E-07	1.1037
CPEdl-P	Fixed(X)	1	N/A	N/A
Rct	Free(+)	50.48	0.29025	0.57498
CPEp-T	Free(+)	0.0037544	4.5247E-05	1.2052
CPEp-P	Fixed(X)	1	N/A	N/A
Rp	Free(+)	195.5	1.2043	0.61601

Chi-Squared:	0.0068513
Weighted Sum of Squares:	1.3497

Data File:	D:\doc\EIS\Exercises\Ch10\1.z
Circuit Model File:	D:\doc\EIS\Exercises\Ch10\3\R(Q(R(QR) mdl
Mode:	Run Fitting / All Data Points (1 - 101)
Maximum Iterations:	100
Optimization Iterations:	0
Type of Fitting:	Complex
Type of Weighting:	Calc-Modulus

Fig. 14.6. Fit of the experimental data 1.z to the model *R*(*C*(*R*(*RC*))) with calculated modulus weighting.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	13.92	0.056154	0.40341
CPEdl-T	Free(+)	1.3355E-05	6.6966E-07	5.0143
CPEdl-P	Free(+)	0.95622	0.0059192	0.61902
Rct	Free(+)	51.47	0.29838	0.57972
CPEp-T	Free(+)	0.0037907	4.1213E-05	1.0872
CPEp-P	Fixed(X)	1	N/A	N/A
Rp	Free(+)	194.9	1.0773	0.55274

Chi-Squared:	0.0050679
Weighted Sum of Squares:	0.99331

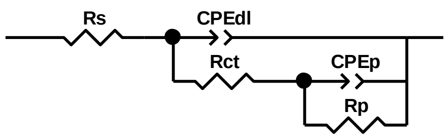
Data File:	D:\doc\EIS\Exercises\Ch10\1.z
Circuit Model File:	D:\doc\EIS\Exercises\Ch10\3\R(Q(R(QR) mdl
Mode:	Run Fitting / All Data Points (1 - 101)
Maximum Iterations:	100
Optimization Iterations:	0
Type of Fitting:	Complex
Type of Weighting:	Calc-Modulus

Fig. 14.7. Results of the fit with CPEdl-P (ϕ_{dl}) as a free parameter.

$$F_{\exp} = \frac{S_1 - S_2}{\dfrac{S_2}{N-p}} = \frac{1.3497 - 0.9931}{\dfrac{0.9931}{196}} = 70.32 \tag{14.6}$$

This value must be compared with the theoretical value of $F(0.05,1,196) = 3.889$ (see Excel file for the determination). As $F_{\exp} >> F(0.05,1,196)$ the addition of the new parameter and replacement of C_{dl} by CPE_{dl} is statistically justified at the confidence level of 95%.

Next, let us check if the replacement of C_{p} by CPE_{p} is justified as well. For this purpose let us run the fit with CPEp-P (ϕ_{p}) as a free parameter. The obtained results are displayed in Fig. 14.8.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	13.94	0.046581	0.33415
CPEdl-T	Free(+)	1.2278E-05	5.2864E-07	4.3056
CPEdl-P	Free(+)	0.96588	0.0050659	0.52449
Rct	Free(+)	50.36	0.27306	0.54222
CPEp-T	Free(+)	0.0039513	3.9998E-05	1.0123
CPEp-P	Free(+)	0.94793	0.0055265	0.58301
Rp	Free(+)	199.7	1.0639	0.53275

Chi-Squared:	0.0033374
Weighted Sum of Squares:	0.65079
Data File:	D:\doc\EIS\Exercises\Ch10\1.z
Circuit Model File:	D:\doc\EIS\Exercises\Ch10\3\R(Q(R(QR) mdl
Mode:	Run Fitting / All Data Points (1 - 101)
Maximum Iterations:	100
Optimization Iterations:	0
Type of Fitting:	Complex
Type of Weighting:	Calc-Modulus

Fig. 14.8. Fit of the experimental data 1.z to the model *R*(*Q*(*R*(*QR*))).

Let us now carry out the F-test for the additional parameter. As the new value of $S_3 = 0.65079$ and the number of free parameters is now 7 the value of F is:

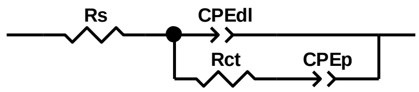
$$F_{\exp} = \frac{S_2 - S_3}{\dfrac{S_3}{N-p_3}} = \frac{0.9931 - 0.65079}{\dfrac{0.65079}{195}} = 102.6 \tag{14.7}$$

As the experimental value exceeds largely the theoretical value $F(0.05,1,195) = 3.89$ addition of CPEp-P and all seven free parameters is statistically justified. It can also be noticed that relative error of CPEdl-T is 4% and all the other parameters 1% or below. However, using calculated proportional weighting the maximal error is only 1.5%.

Exercise 14.4.

Fit 4.z into the model $R_{\mathrm{s}}(C_{\mathrm{dl}}(R_{\mathrm{ct}}C_{\mathrm{p}}))$. Check if the use of the CPE elements instead of capacitances is statistically justified.

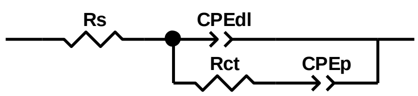
Let us build a more general model containing already CPE elements: $R(Q(RQ))$ and read in data: 4.z. Then, the initial values of the parameters must be guessed, for example as in Fig. 14.9.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	5	N/A	N/A
CPEdl-T	Free(+)	1E-05	N/A	N/A
CPEdl-P	Free(±)	1	N/A	N/A
Rct	Fixed(X)	50	N/A	N/A
CPEp-T	Fixed(X)	0.001	N/A	N/A
CPEp-P	Fixed(X)	1	N/A	N/A

Fig. 14.9. Equivalent electrical model $R_s(Q_{dl}(R_{ct}Q_p))$ with the initial guess of the parameters.

Next, the fit must be run to the simpler model $R(C(RC))$ by fixing the values of the CPE exponent. The result is shown in Fig. 14.10.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	2.044	0.0081785	0.40012
CPEdl-T	Free(+)	1.8091E-05	4.121E-08	0.22779
CPEdl-P	Fixed(X)	1	N/A	N/A
Rct	Free(+)	50.18	0.078153	0.15575
CPEp-T	Free(+)	0.014914	6.1867E-05	0.41482
CPEp-P	Fixed(X)	1	N/A	N/A

Chi-Squared:	0.00049497
Weighted Sum of Squares:	0.098005

Data File:	D:\doc\EIS\Exercises\Ch10\4\2.z
Circuit Model File:	D:\doc\EIS\Exercises\Ch10\4\R(Q(RQ)).r
Mode:	Run Fitting / All Data Points (1 - 101)
Maximum Iterations:	100
Optimization Iterations:	0
Type of Fitting:	Complex
Type of Weighting:	Calc-Modulus

Fig. 14.10. Fit of the experimental data 4.z to the model *R*(*C*(*RC*)) using calculated modulus weighting.

Looking at the fit, Fig. 14.11, it is obvious that the low frequency data are poorly approximated and systematic differences exist between the approximation and the experimental data. In the next model C_p was replaced by CPEp by adding one free parameter CPEp-P. The results are shown in.

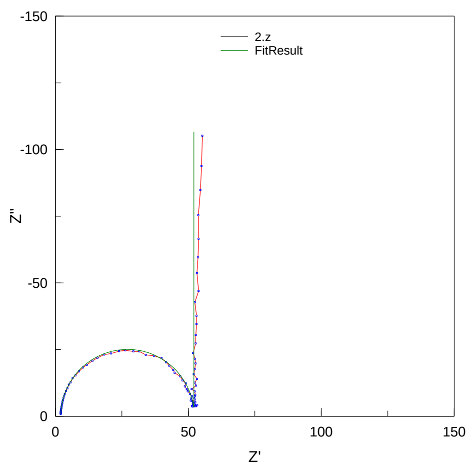
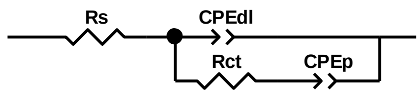


Fig. 14.11. Results of the fitting data in 4.z to the model *R*(*C*(*RC*)), Fig. 14.10.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	2.043	0.0068917	0.33733
CPEdl-T	Free(+)	1.8085E-05	3.4763E-08	0.19222
CPEdl-P	Fixed(X)	1	N/A	N/A
Rct	Free(+)	49.88	0.073387	0.14713
CPEp-T	Free(+)	0.014985	5.3315E-05	0.35579
CPEp-P	Free(+)	0.97909	0.0023188	0.23683

Chi-Squared:	0.00034784
Weighted Sum of Squares:	0.068524
Data File:	D:\doc\EIS\Exercises\Ch10\4\2.z
Circuit Model File:	D:\doc\EIS\Exercises\Ch10\4\R(Q(RQ)).r
Mode:	Run Fitting / All Data Points (1 - 101)
Maximum Iterations:	100
Optimization Iterations:	0
Type of Fitting:	Complex
Type of Weighting:	Calc-Modulus

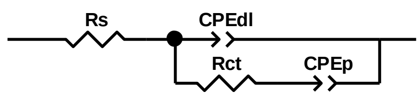
Fig. 14.12. Results of the fit of 4.z to *R*(*C*(*RQ*)) model.

The new plot seems to be very good, see Ex14-4.xlsx, but to be sure that the new parameter is important the *F*-test must be carried out:

$$F_{\text{exp}} = \frac{0.098005 - 0.068524}{\dfrac{0.068524}{202-5}} = 87.76 \tag{14.8}$$

This value must be compared with the theoretical value of $F(0.05,1,197)$= 3.889. As $F_{exp} >> F(0.05,1,197)$ addition of the new parameter is statistically justified at the assumed confidence level of 95% this is the better model.

However, only by looking at the complex plane and Bode plots it is impossible to decide if it is justified to use CPE element instead of the double layer capacitance. To test it another free parameter CPEdl-P was added and the approximation carried out. The results are shown in Fig. 14.13.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	2.002	0.0059284	0.29612
CPEdl-T	Free(+)	1.9894E-05	1.4624E-07	0.7351
CPEdl-P	Free(+)	0.98868	0.00085862	0.086845
Rct	Free(+)	50.17	0.058371	0.11635
CPEp-T	Free(+)	0.014978	3.8966E-05	0.26015
CPEp-P	Free(+)	0.98275	0.001719	0.17492

Chi-Squared:	0.00018363
Weighted Sum of Squares:	0.035992

Data File:	D:\doc\EIS\Exercises\Ch10\4\2.z
Circuit Model File:	D:\doc\EIS\Exercises\Ch10\4\R(C(RC)).r
Mode:	Run Fitting / All Data Points (1 - 101)
Maximum Iterations:	100
Optimization Iterations:	0
Type of Fitting:	Complex
Type of Weighting:	Calc-Modulus

Fig. 14.13. Results of the fit of data in 4.z to the electrical equivalent model *R*(*Q*(*RQ*)).

The F-test must be repeated again:

$$F_{\mathrm{exp}} = \frac{0.068524 - 0.035992}{\dfrac{0.035992}{202-6}} = 177.2 \tag{14.9}$$

Again, $F_{\mathrm{exp}} >> F(0.05,1,196)$ and the new model is statistically justified. One can also notice that the relative standard deviations of the obtained parameters are 0.7% or less. In conclusion the best model is $R(Q(RQ))$.

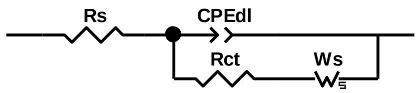
Exercise 14.5.

Fit the data in 5.z to the model $R(C(RW\mathrm{s}))$ where W_s is the transmissive mass transfer impedance. Check if the use of the CPE element is justified.

First, read the data file 5.z into ZView and prepare the circuit. Then the initial values must be given to the parameters. Just looking at the plot one can guess the values of R_s and R_{ct} (radius of the first semicircle). It is impossible to guess the values of the double layer capacitance from the complex plane plot but a value of 10 μF was used. It is also very difficult to guess the values of the finite-length transmissive mass transfer impedance: W_s-R and W_s-T:

$$Z_{\mathrm{W_s}} = R\frac{\tanh(j\omega T)^{\phi}}{(j\omega T)^{\phi}} \tag{14.10}$$

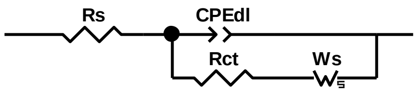
where $\phi = 0.5$. The values of R and T were assumed as 1, see the Fig. 14.14. All these results can be inspected in Ex14-5.xlsx.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	25	N/A	N/A
CPEdl-T	Free(+)	1E-05	N/A	N/A
CPEdl-P	Fixed(X)	1	N/A	N/A
Rct	Free(+)	50	N/A	N/A
Ws-R	Free(+)	1	N/A	N/A
Ws-T	Free(+)	1	N/A	N/A
Ws-P	Fixed(X)	0.5	N/A	N/A

Fig. 14.14. Equivalent electrical model $R_s(Q_{dl}(R_{ct}W_s))$ with the initial guess of the parameters.

After running the fit with CPEdl-P = 1 and Ws-P = 0.5 fixed the following results obtained are shown in Fig. 14.15. The results seem to be correct and the standard deviations of the parameters are low. However, let us see if the use of Ws-P as a free parameter could improve the fit. The results are shown in Fig. 14.16. There is small improvement in the sum of squares, but the value of $F_{ex} = 0.762$, much smaller from the theoretical value $F(0.05,1,196) = 3.89$ (see Ex14-5.xlsx). This means that there is no statistically important improvement and the parameter Ws-P should be fixed as 1. Similarly, after setting CPEdl-P free no improvement is observed. In fact, there is a very small increase in the sum of squares related to the numerical errors. In conclusion, the model $R_s(C_{dl}(R_{ct}W_s))$ and Ws-P = 0.5, Fig. 14.15, is the best.

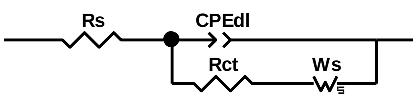


Element	Freedom	Value	Error	Error %
Rs	Free(+)	24.94	0.02958	0.1186
CPEdl-T	Free(+)	1.9898E-05	9.0477E-08	0.4547
CPEdl-P	Fixed(X)	1	N/A	N/A
Rct	Free(+)	50.04	0.10494	0.20971
Ws-R	Free(+)	40.12	0.22875	0.57016
Ws-T	Free(+)	10.18	0.16787	1.649
Ws-P	Fixed(X)	0.5	N/A	N/A

Chi-Squared: 0.0012184
Weighted Sum of Squares: 0.24003

Data File: D:\doc\EIS\Exercises\Ch10\5\3.z
Circuit Model File: D:\doc\EIS\Exercises\Ch10\5\R(Q(RW)).
Mode: Run Fitting / All Data Points (1 - 101)
Maximum Iterations: 100
Optimization Iterations: 0
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Fig. 14.15. Results of the fit of 3.z into the circuit $R_s(C_{dl}(R_{ct}W_s))$.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	24.94	0.029654	0.1189
CPEdl-T	Free(+)	1.9895E-05	9.0863E-08	0.45671
CPEdl-P	Fixed(X)	1	N/A	N/A
Rct	Free(+)	50	0.12716	0.25432
Ws-R	Free(+)	40.22	0.29006	0.72118
Ws-T	Free(+)	10.25	0.21134	2.0619
Ws-P	Free(+)	0.49744	0.0047735	0.95961

Chi-Squared: 0.0012199
Weighted Sum of Squares: 0.2391

Data File: D:\doc\EIS\Exercises\Ch10\5\3.z
Circuit Model File: D:\doc\EIS\Exercises\Ch10\5\R(Q(RW)).
Mode: Run Fitting / All Data Points (1 - 101)
Maximum Iterations: 100
Optimization Iterations: 0
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Fig. 14.16. Results of the fit with Ws-P as a free parameter.

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