### **AUTOLAB APPLICATION NOTE**

# AC Voltammetry at High Frequencies by using the FRA2 module

In some applications it is necessary to perform AC voltammetry at frequencies higher than 250 Hz, which is the limit for this technique in the GPES software. This short note shows how these experiments can be done with the aid of the Autolab and the FRA2 module.

#### AC Voltammetry in GPES software

In AC voltammetry, the potential is stepped while at every step value a sine wave is applied, as shown in the figure below.



The Edit Procedure Window in Figure 1 shows the parameters for a typical experiment in which the potential is stepped from -1.2 to 0.05 V with a step of 5 mV. At every step during the last 0.3 s (Modulation Time) a sine wave of 66 Hz is applied. The result in this case is measured without phase sensitivity, meaning that both the resistive as well as the capacitive contributions will be visible.

The technique implemented in the GPES software only allows a frequency range for the sine wave of 1-250 Hz. In combination with the FRA2 module, the same experiments can be done [1], with the advantage that the frequency range now run from 10  $\mu$ Hz to 1MHz. The set up of such an experiment is described below.

#### AC voltammetry in FRA software

By using the potential scan option in the FRA software it is possible to do AC voltammetry. The basic parameters for such an experiment are shown in the Edit Procedure window in Figure 2.

The parameters defined are for n experiments where the potential is scanned from 0 to 1 V with 50 mV step potential. The frequency that needs to be applied at the end of every step can be defined in the Edit Frequencies window.

The window shown is for an experiment with a frequency of 1000 Hz and amplitude of 50 mV. Normally when the FRA software is used, the sine wave is applied during the complete time of the potential step. In cases where this is unwanted, the option "Repeat pre-treatment before every" in the Edit Procedure window should be changed from "no" to "every frequency scan".

Finally in the FRA manual control window as shown in Figure 3, it is possible to define parameters similar to the "Modulation Time" in the GPES software. There are two possibilities:

• The integration time

This is the minimum period during which the signals are measured. This value is equal to the Modulation time in the GPES software.

• The minimum number of cycles to integrate.

This is the minimum number of ac signal periods during which the signals are measured. The more periods, the more accurate is the result. The minimum is one cycle. This value is only useful for low frequency measurements.

The AC voltammetry measurements in GPES are shown as current vs. potential whereas in the FRA software they are in the form of impedance vs. potential. In the data presentation window of the GPES software the user has the option of saving the impedance data by using the "Save Impedance Data" in the "File" pull down menu, and thus compare with the results from FRA software.

#### References

1. C, Hortholary, F. Minc, C. Coudret, J. Bonvoisin and J.-P. Launay, "A new redox site as an alternative to ferrocene to study electron transfer in self-assembled monolayers," *Chem. Commun.*, **17**, 1932 – 1933 (2002).

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**Figure 1:** Edit procedure window for AC voltammetry in GPES software.

🛃 Edit procedure		
Send		
Page 1	Page 2	<u> </u>
Pretreatment		
Conditioning potential (V) :	0	
Duration (s) :	0	
Deposition potential (V) :	0	
Duration (s) :	0	
Equilibration time (s) :	5	
Measurement		
Cell off after measurement :	×	
Modulation time (>= 0.01 s):	.3	
$\frac{1}{2} = \frac{1}{2} = \frac{1}$	0. <mark>272</mark>	- 11
Phace consitive :		
Phase (-180* - 180*):	0	
Potentials		
Initial potential (V) :	-1.2	
End potential (V):	.05	
Step potential (V) :	.0051	
Amplitude (0.001 - 0.3 Vrms) :	.005	¥

Figure 2: Edit procedure window in FRA software.

Figure 3: Edit frequency window in FRA software.

Edit <u>f</u> requencies		
Page 1	Page 2	
Pretreatment		
First conditioning potential (V):	.1	
Duration (s):	0	
Equilibration time (s):	2	
Repeat pretreatment before		
every:	no 💌	
Measurement		
A.C. mode:	single sine 💌	
Cell off after measurement:	×	
Standby potential (V):	0	
Define potentials w.r.t. OCP:		
Time to wait for OCP (s):	0	
Potentials		
Start potential (V):	0	
End potential (V):	1	
Step potential (V):	.05	

Para	meters			
Subs	cans ; B	egin frequency : 1000.0	Hz	Distribution :
Sub	scan 1	End frequency : 1000		🔿 Linear
Sub	scan 2 scan 3	Number of freq. : 1		O Square root
Sub Sub	scan 4 scan 5	Amplitude (rms) : .05		Content Con
C <u>a</u>	culate Minimu frequer	m time of measurement for hcy scan (hh:mm:ss) :	one O	0:00:03
Nr	Frequency (Hz)	Amplitude (V)	1	
1	1000.004	.05000		

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