

DigiElch 7™ from ElchSoft is a simulation program for electrochemical experiments. DigiElch 7 offers a number of unique features compared to available electrochemical simulation programs:

- Fitting multiple data files to a mechanism to extract kinetic and thermodynamic properties.
- Modeling of termolecular charge transfer reactions such as the proton coupled electron transfer.
- Exact 2-D simulation of band and disk microelectrodes.
- ChronoAmperometry, Square Wave Voltammetry, Impedance Spectroscopy, Fourier Transform Voltammetry, in addition to Cyclic Voltammetry
- Simulation of amalgam formation with mercury electrodes
- Modeling surface adsorption and reactions of adsorbed species.
- An optional adaptive grid algorithm.
- Improved computational efficiency via parallel processing.

DigiElch 7 simulates user-defined mechanisms consisting of an arbitrary number of charge transfer steps and (first- or second-order) chemical reactions. An extended Frumkin isotherm is used to model the adsorption processes of reactants, products or intermediate chemical species. DigiElch 7 also brings the unique ability to simulate electron transfer reactions that are termolecular (such as the proton coupled electron transfer). All simulations account for effects such as IR-drop and/or double layer charging. Simulations and fitting take advantage of multi-core processors with full control during setup.

The end result of any simulation is a plot of current vs. voltage or time or a plot of impedance vs. frequency. Concentration distance and surface concentration potential curves (as well as surface coverage potential curves) are also available.

DigiElch 7 comes in two varieties:

**DigiElch-Standard:** Experimental data can be imported and compared with a simulation

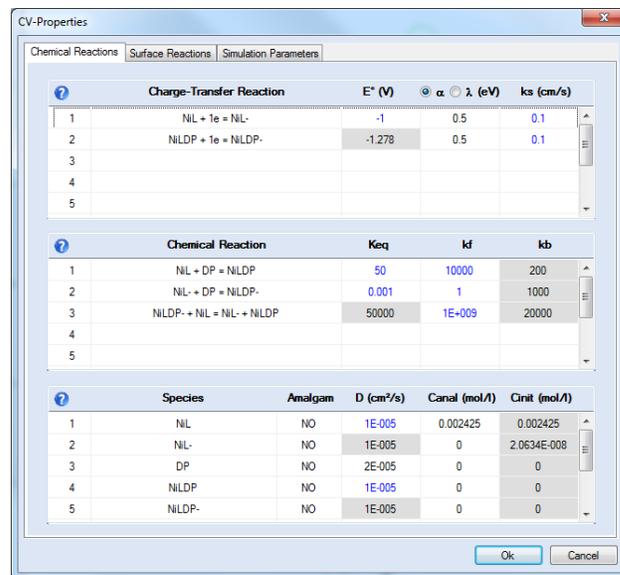
**DigiElch-Professional:** Multiple experiments employing different analytical concentrations and experimental parameters (e.g sweep rate, switching potential) can be imported and fit to the same model to get reliable kinetic and thermodynamic properties.

In addition, DigiElch 7 has the option of using a Gamry Reference 600 to acquire data. Either variety (Standard or Professional) can be expanded to include the experimental modules at little extra cost.

### Chemistry & Electrochemistry Setup

DigiElch 7 can handle an arbitrary number of reactions and species. The electrochemical system is defined by the charge transfer reactions, the coupled chemical reactions and the initial concentrations of the species in solution.

Kinetics of the system can obey either Butler-Volmer (BV) or Marcus equations. The BV equation requires a transfer coefficient ( $\alpha$ ) and Marcus equation requires the reorganization energy ( $\lambda$ ). BV kinetics can be setup for single or multi-electron transfer. Left-clicking on any of the charge transfer reactions on the parent setup screen brings up the charge transfer reaction setup dialog box.



The screenshot shows the 'CV-Properties' dialog box with three tabs: 'Chemical Reactions', 'Surface Reactions', and 'Simulation Parameters'. The 'Charge-Transfer Reaction' tab is active, showing a table with 5 rows. The first two rows are selected. Below this is a 'Chemical Reaction' table with 5 rows, and a 'Species' table with 5 rows. The 'Species' table includes columns for Amalgam, D (cm²/s), C<sub>anal</sub> (mol/l), and C<sub>init</sub> (mol/l).

Charge-Transfer Reaction	E° (V)	$\alpha$	$\lambda$ (eV)	k <sub>s</sub> (cm/s)
1. NIL + 1e = NIL-	-1	0.5	0.1	0.1
2. NILDP + 1e = NILDP-	-1.278	0.5	0.1	0.1
3.				
4.				
5.				

Chemical Reaction	K <sub>eq</sub>	k <sub>f</sub>	k <sub>b</sub>
1. NIL + DP = NILDP	50	10000	200
2. NIL- + DP = NILDP-	0.001	1	1000
3. NILDP- + NIL = NIL- + NILDP	50000	1E+009	20000
4.			
5.			

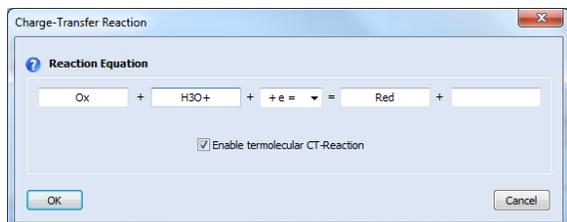
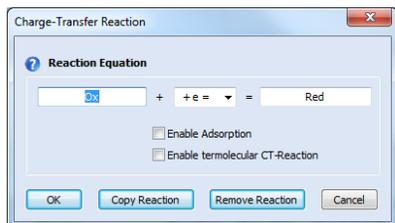
  

Species	Amalgam	D (cm²/s)	C <sub>anal</sub> (mol/l)	C <sub>init</sub> (mol/l)
1. NIL	NO	1E-005	0.002425	0.002425
2. NIL-	NO	1E-005	0	2.0634E-008
3. DP	NO	2E-005	0	0
4. NILDP	NO	1E-005	0	0
5. NILDP-	NO	1E-005	0	0

**Typical Parent Setup Screen of an ECE System.** The chemistry and the electrochemistry of the system can be defined through the parent setup screen.

The rate constants will be calculated based on the selections and the parameters entered in the parent dialog box.  $k_f$  or  $k_b$  can be forced to be zero by choosing irreversible reactions.

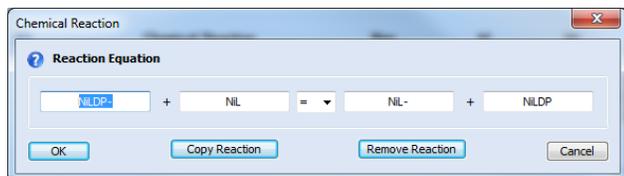
If the termolecular CT-Reaction is enabled, the dialog box changes to specify the same. The most notable family of reactions of this type is the proton coupled electron transfer (PCET) reactions. DigiElch 7 is the first commercial software package that can simulate PCET reactions.



**Reaction Setup Dialog Box** The reactions can be fully reversible or irreversible with multiple electrons. If “Enable Adsorption” is selected, the “Surface Reactions” tab will be enabled. If the “Enable termolecular CT-Reaction” toggle is selected, the dialog box changes to the second box above.

If adsorption is enabled, the “Surface Reactions” tab in the parent setup screen will be enabled, which will be discussed in the next section.

?	Chemical Reaction	Keq	kf	kb
1	NL + DP = NLDP	50	10000	200
2	NL + DP = NLDP-	0.001	1	1000
3	NLDP- + NL = NL + NLDP	50000	1E+009	20000
4				
5				



**Chemical Reaction Setup Dialog Box** The chemical reactions can be setup as unimolecular or bimolecular reactions using any chemical species of choice.

Left clicking any of the chemical reactions will bring up the chemical reaction setup dialog box shown above. The thermodynamic and the kinetic parameters of a given chemical reaction (i.e.,  $K_{eq}$ ,  $k_f$ ,  $k_b$ ) need to be entered in the parent setup screen. Due to the mathematical dependence of the variables,  $K_{eq}$  and  $k_f$  can be individually manipulated and  $k_b$  is calculated from those two.

?	Species	Amalgam	D (cm <sup>2</sup> /s)	Conal (mol/l)	Cinit (mol/l)
1	NIL	NO	1E-005	0.002425	0.002425
2	NL-	NO	1E-005	0	2.0634E-008
3	DP	NO	2E-005	0	0
4	NLDP	NO	1E-005	0	0
5	NLDP-	NO	1E-005	0	0

**Bottom Part of the Parent Setup Screen** The diffusion coefficients and the analytical concentrations of the chemical species can be adjusted. The initial concentrations are calculated depending on the pre-equilibria preference discussed later.

### Adsorption and Surface Reactions Setup

DigiElch 7 can simulate adsorption processes and surface reactions with unprecedented detail. The adsorption-desorption reaction is defined through an equilibrium constant ( $K^*$ ), an adsorption rate constant ( $k_f^*$ ) and an interaction parameter ( $a^*$ ). The model is implemented such that, in equilibrium, the Frumkin isotherm is recovered.

CV-Properties					
Chemical Reactions		Surface Reactions		Simulation Parameters	
CT-Reaction of Adsorbed Species					
?		E* (V)	$\alpha^*$	$ks^*$ (1/s)	
1	Ox* + e = Red*	0	0.5	0	
2					
3					
Adsorption Reaction					
?		K*	$kf^*$	$a^*$	
1	Ox = Ox*	100	10	0	
2	Red = Red*	100	10	1	
3					
Reaction of Adsorbed Species					
?		Keq	$kf$	$kb$	
1					
2	Cancel				
3	Add Type I: Red1* + Ox2 = Ox1* + Red2				
3	Add Type II: A* + P = Q + S				
Adsorbed Species					
?		Cinit (mol/l)	$\Gamma^*$ max	$\Theta$	
1	Ox*	0.001	1E-010	0.090909	
2	Red*	0	1E-010	0	
3					
4					

**Surface Reactions Setup Tab** DigiElch 7 can be used to simulate adsorption-desorption and surface reactions with unprecedented detail.

Charge transfer equations of the adsorbed species can also be modeled. The equilibrium potential for the adsorbed redox reaction is not free and is calculated using the equilibrium constant for adsorption and the redox potential of the corresponding dissolved species.

Two types of chemical reactions involving adsorbed species can be simulated:

Type I:  $Red1^* + Ox2 = Ox1^* + Red2$

Type II:  $A^* + P = Q + S$

Both types of reaction are widely applicable in areas like heterogeneous catalysis and bioelectrochemistry.

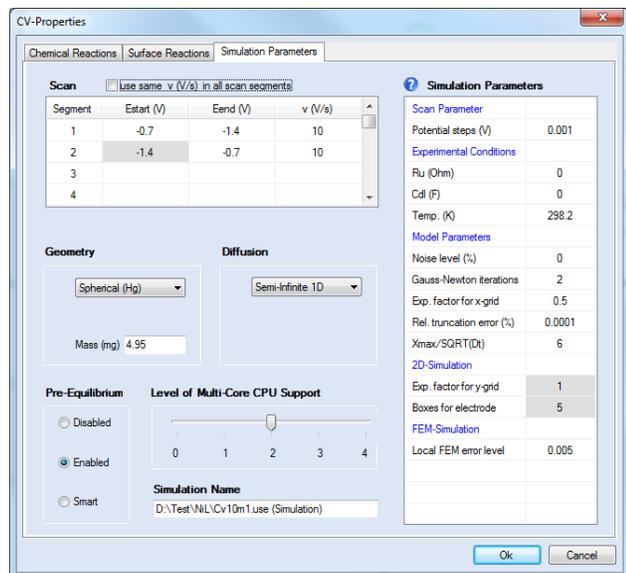
## Experiment Setup

In the setup window, the experimental waveform can be specified (details will follow in the relevant sections). The rest of the parameters in this window are common to all experiments. They control experimental and computational details. The pre-equilibrium option establishes the initial concentrations at the starting potential (which may or may not be different from the analytical concentrations). The three available options are:

**Disabled:** No calculations are performed. The analytical concentrations are used as initial concentrations. Ideal for experiments where solution is prepared and the experiment is started at the initial potential without any time for the solution and the electrodes to equilibrate.

**Enabled:** The initial concentrations are calculated using the Nernst Equation for the electrochemical reactions and the equilibrium equation for chemical reactions. Ideal for experiments where the solution is given enough time to fully come to equilibrium at the initial potential.

**Smart:** Nernst Equation is not used but the analytical concentrations are reassigned depending on the initial potential and the standard potentials. The initial concentrations are then calculated using the chemical equilibria with the analytical concentrations. This is a more realistic calculation since there is not enough time for a full equilibrium to establish in real experiments.



**Setup Screen for the Simulation Parameters** Electrode geometry, dimensionality, pre-equilibria, and a range of computational parameters

The geometry of the electrode can be varied from planar to spherical for 1-D simulations and between band and disk for 2-D simulations. For a spherical mercury electrode, the amalgam formation process can

also be modeled for any of the species involved in the simulation.

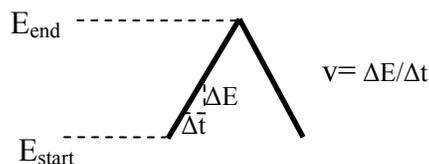
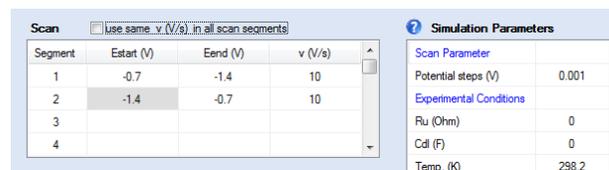
A thin layer cell is simulated by changing the diffusion option to finite 1-D and specifying the length of the cell. The boundary condition at the far end of the cell can be individually specified to be either ORB (Open Right Boundary) or BRB (Blocked Right Boundary). ORB fixes the concentration gradient to be zero and BRB fixes concentration to be  $C_{init}$  at the far end of the cell.

There are a number of computationally critical parameters that determine the balance between performance and accuracy of the simulations. The default parameters are chosen for accurate simulations that are reasonably fast. Detailed information on these parameters can be found under the help menu of the program.

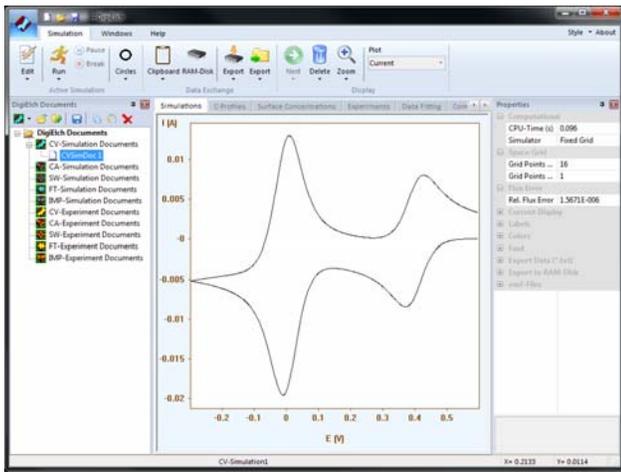
Additionally, the effects of uncompensated resistance and double layer capacitance can be investigated. Both these effects can be a real nuisance in a number of experiments and even dominate the response in faster experiments. Using DigiElch 7 the effect can be predicted and compared with the expected result of any electrochemical system. The effects of temperature can also be easily investigated.

## Cyclic Voltammetry (CV) Simulations

Cyclic Voltammetry (CV) is commonly the first experiment performed in any physical electrochemical study. Potential is swept over a wide range in search of redox couples. Once found, the redox couple is investigated with varying sweep rates, scan limits, and analytical concentrations. The simulation parameters for CV include an independently adjustable sweep rate for every segment of the sweep, the scan limits of each segment, and the size of the potential steps between data points. Copying the  $E_{start}$  value for a segment from the  $E_{end}$  value from the previous segment keeps the entire experiment continuous.



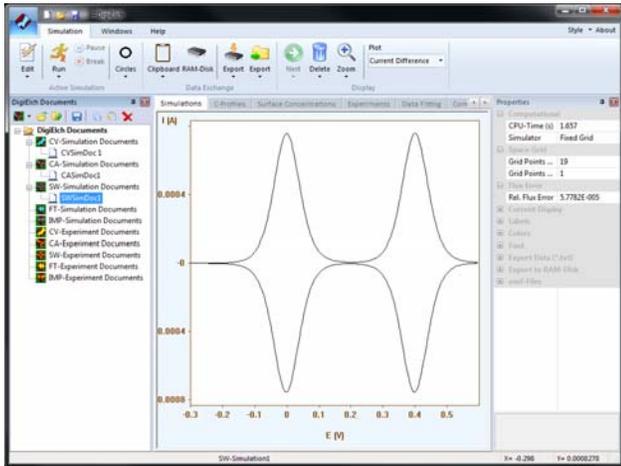
**CV setup and anatomy of the CV signal** Three parameters define the signal.  $E_{start}$ ,  $E_{end}$ , and sweep rate are available on the setup screen as shown.



**CV simulations** The simulations can include adsorbed species as well as species diffusing from solution.

### Square Wave Voltammetry (SWV) Simulations

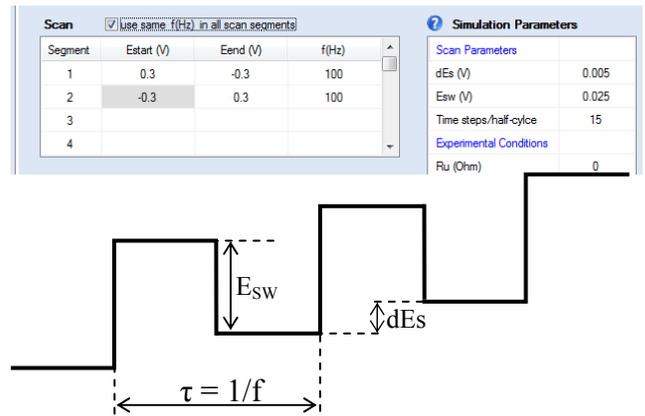
Square Wave Voltammetry (SWV) is routinely employed to suppress the background current in cyclic voltammetry



**SWV simulation and concentration profiles** Square waves and concentration profiles can also be simulated with any of the systems described in the CV section.

Its ability to discriminate against slow events in favor of fast ones can be used to separate multiple redox events occurring at the same potential. DigElch 7 can simulate SWV experiments in any of the systems explained before; there is no restriction on the geometry or the chemistry.

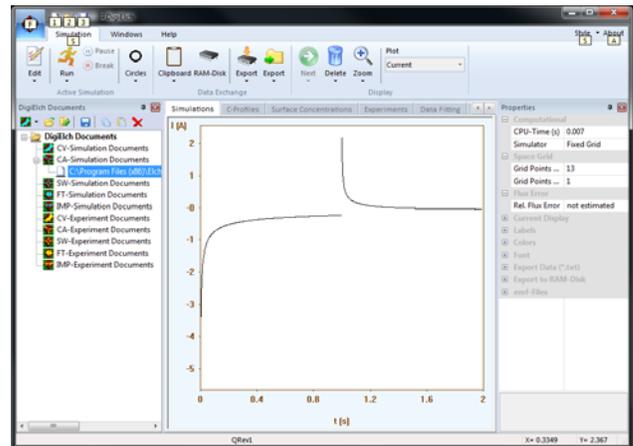
A square wave signal as shown in the figure below is applied and the current measurements are taken at the middle ( $\tau/2$ ) and the end of every period ( $\tau$ ). This way the capacitive background currents decay and a more direct measurement of the faradaic current is possible.



**SWV scan setup and anatomy of the SWV signal** Three parameters define the signal.  $f$ ,  $dE_s$  and  $E_{sw}$  are available on the setup screen.

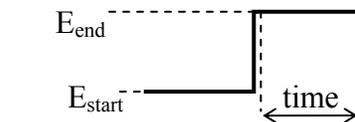
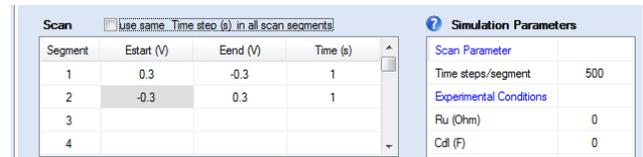
The setup of the square wave is also divided into segments much like the CV experiments. A separate frequency  $f$  and potential limits can be specified for each segment.

### ChronoAmperometry (CA) Simulations



**CA simulation and concentration profiles**

ChronoAmperometry and concentration profiles can also be simulated with any of the systems described in the CV section



**CA setup and anatomy of the CA signal** Three parameters define the signal.  $E_{start}$ ,  $E_{end}$  and time are available on the setup screen as shown.

ChronoAmperometry (CA) involves holding the potential constant for a period of time while the current is measured.

At the end of the time period the potential is stepped to a new value and the current measurement continues. The waveform and the setup parameters are shown in the figure below.

In the CA setup screen, the potentials and the time intervals of the segments can be independently specified.

### Multi-Sine Impedance (IMP) Simulations

Electrochemical Impedance Spectroscopy can be simulated using a multiple sine excitation. A multi-sine voltage signal is applied to the system and the resulting current is simulated as shown in the figure. The impedance spectrum is then calculated by a Fourier transform of the time signal. The calculated impedance can be fully or partially corrected for IR effects.

The AC simulation starts with a constant potential preconditioning step. The initial concentrations are calculated to be in equilibrium at  $E_{start}$  and then the potential is stepped to  $E_{dc}$  for the specified duration.

At the end of the DC experiment, the AC-Signal is applied. The definition of the AC signal involves the fundamental amplitude ( $dE_{ac}$ ), the number of AC-Packets, the number of applied frequencies (up to 15), and the fundamental frequency ( $f_{min}$ ). The maximum frequency is calculated using the signal definition and cannot be modified. The signal applied will be composed of AC-Packets that are  $f_{min}^{-1}$  in length.

DC-Signal	AC-Signal	Simulation Parameters
Estart (V) 0.3	dEac (V) 0.015	AC-Signal Parameters
E <sub>dc</sub> (V) 0	AC-Packets 2	log2(Data Points) 11
DC-Time (s) 5	f <sub>min</sub> (Hz) 100	Applied Frequencies 15
Define AC-Signal Components	f <sub>max</sub> (Hz) 5050	Experimental Conditions
		R <sub>u</sub> (Ohm) 0
		C <sub>d</sub> (F) 0

**IMP setup** The simulated IMP experiment can be setup with a DC conditioning step before the AC experiment.  $E_{start}$ ,  $E_{dc}$  and DC-Time relate to the conditioning step, while details of the IMP experiment are given in the AC-Signal box.

Individual AC-Packets can be defined by assigning phase and amplitude to each component using the "Define Signal" button. When defining the signal, the frequency and the amplitudes are assigned relative to the corresponding fundamental parameter in the parent dialog box. The signal generated in this way is then adjusted such that the maximum value of the amplitude becomes equal to the value entered for  $dE_{ac}$ .

The real and imaginary impedances ( $Z_r$  and  $Z_i$ ) can be displayed in three ways:  $Z_i$  and  $Z_r$  vs  $1/\sqrt{\omega}$ ,  $\cot(\phi)$  vs.  $\sqrt{\omega}$ , and  $Z_i$  vs.  $Z_r$ , where  $\cot(\phi)$  is the cotangent of the phase angle(i.e.,  $Z_i/Z_r$ ) and  $\omega$  is the angular frequency (i.e.,  $2\pi f$ ).

Define AC-Signal Components . . .

**Amplitude Settings**

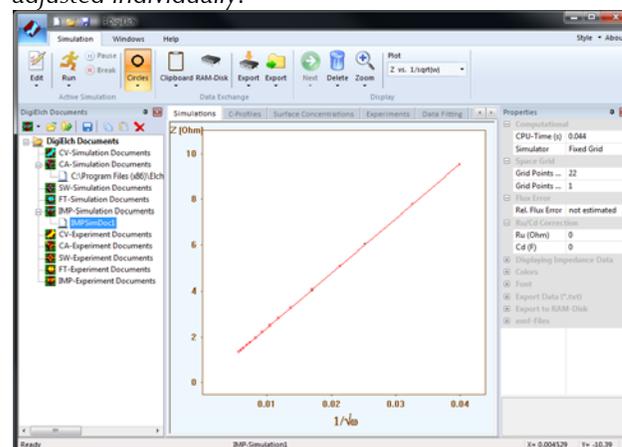
Set relative amplitude equal to 1 for each frequency  
 Set relative amplitude equal to 1/sqrt(f)  
 Set relative amplitude individually for each frequency

Index, i	f(i)/f <sub>0</sub>	Phi(i)	A(i)/A <sub>1</sub>
1	2	1.32	1
2	3	1	1
3	5	3.9	1
4	7	0.53	1
5	11	2.98	1
6	17	2.39	1
7	23	4.65	1
8	29	0.69	1
9	37	6.1	1
10	47	3.56	1
11	59	5.2	1
12	67	5.92	1
13	79	1.4	1
14	89	1.41	1
15	101	0	1

f = frequency, Phi = phase angle, A = Amplitude

OK Reset Default Signal Cancel

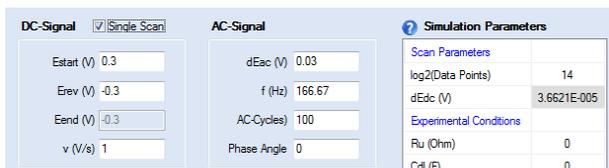
**IMP signal definition** The signal can be defined with up to 15 components with individual frequencies phases and amplitudes. The amplitudes can be fixed to the fundamental amplitude, defined to be  $1/\sqrt{f}$ , or adjusted individually.



**IMP simulation and IR correction** Impedance spectroscopy can be simulated with any of the systems.

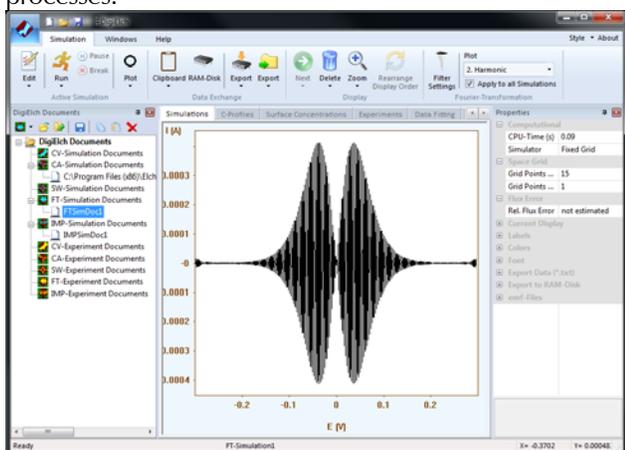
### Fourier Transform Voltammetry (FT) Simulations

Fourier transform voltammetry enables the DC and AC interrogation of electrochemical processes along with the second and third harmonic AC response when high AC amplitudes are employed. The excitation waveform is a linear ramp with a single frequency sine wave superimposed. Once the current is measured, a transform to the frequency domain is performed to calculate DC, AC and higher harmonics. The time domain signal is then investigated separately for DC, AC and the higher harmonics.



**FT Setup parameters** The setup for fourier transform CV includes the setup parameters of the cyclic voltammetry along with the AC-signal.

The simulation results in plots of current vs. voltage for the DC and the various harmonics. The higher harmonics are useful for studies of electrode kinetics due to emergence of fingerprint behaviors for given processes.



**FT Simulation result** The result of the simulation provides the DC current as well as the fundamental and higher harmonic AC response. Concentration and Coverage Profiles

Concentration gradients and surface coverages are the centerpiece of any electrochemical experiment. For species diffusing to the electrode, the current is given by Fick's first law of diffusion. A side by side view of concentration profiles with the CV curve aids the interpretation of complex systems and provides a useful teaching tool for simple systems.

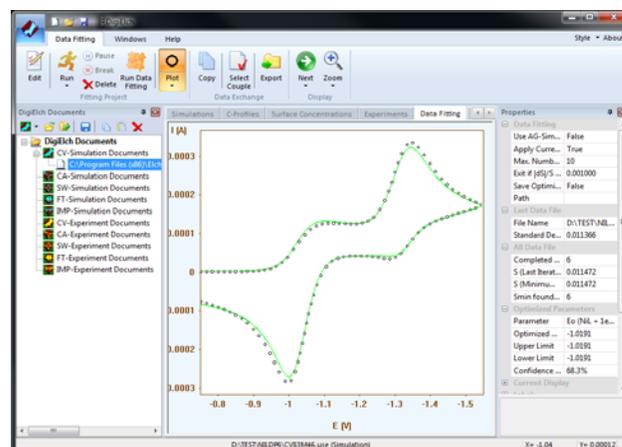
### Experimental Data Fitting (DigiElch-Professional Only)

Using DigiElch Professional a non-linear least squares fitting algorithm can be simultaneously applied to multiple experimental curves simultaneously. One can use multiple data files taken with different analytical concentrations and experimental parameters (e.g. scan rate and scan limits for cyclic voltammetry) that all fit to the same mechanism.

The parameters to be fit can be chosen to be any or all of:

- redox potentials ( $E^0$ )
- transfer coefficients ( $\alpha$ )
- rate constants ( $k_f$ )
- rate constants ( $k_b$ )
- rate constants ( $k_c$ )
- equilibrium constants ( $K_{eq}$ )
- diffusion coefficients ( $D$ )

Diffusion coefficients of two or more species can be kept identical throughout the fitting procedure.



**Data fitting** A group of data files, imported into DigiElch can be fit to a mechanism.

### Multitasking and Parallel Processing Support

Modern computers employ multi-core processors for more efficient computation. DigiElch 7 employs parallel processing at five separate user controlled levels. This allows the user immense control over the resources of the computer and the time it takes to run the fitting routines.

At the maximum parallelization level, the computation time can decrease by factors of two and four for dual core and quad core CPUs respectively.

DigiElch 7 can run multiple simulations and fittings at the same time. Different simulation documents can be processed to run simulations of different types concurrently.

### Data Acquisition

DigiElch 7 has a special module that allows it to interface with the Reference 600 potentiostat to be able to acquire data\*. The experiment is subject to instrument limitations regarding speed and precision, but there is no limit on the type of measurement. Any experiment that can be simulated, can also be performed through the instrument.

### System Information

DigiElch 7 requires 32- or 64-bit version of Windows XP, Windows Vista or Windows 7. The efficiency of the simulations and fitting strongly depend on the specifics of the computer. DigiElch is compatible with data taken using Gamry Instruments PHE200 and PV220 systems. It may also be compatible with other data formats. Contact Gamry Instruments regarding other data formats.

\* DigiElch Reference 600 module needs to be purchased separately.

