

Electrochemical Impedance Spectroscopy

GAMRY
INSTRUMENTS

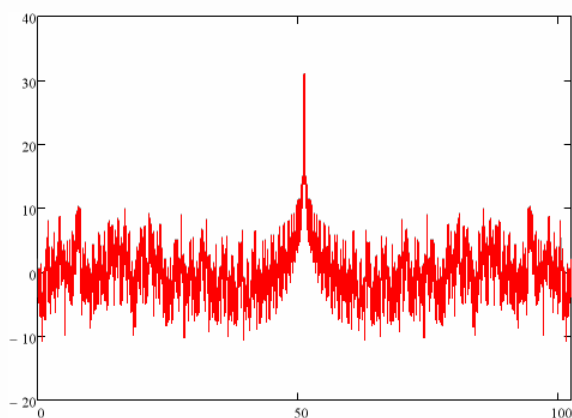
Outline

- OptiEIS – Smarter multisine
 - Phase optimization
 - Amplitude optimization
- Autofit
 - Intelligent fitting needs no knowledge of equivalent circuit values
- Equipment

Most commonly, EIS is measured using a “single-sine” method where individual frequencies are measured sequentially. One disadvantage of single-sine EIS is the time it takes to acquire a full spectrum. A complete sine wave cycle takes ~17 min at 1 mHz and ~27 hrs for 10 μ Hz. This disadvantage can be overcome by measuring multiple frequencies at the same time (akin to Fourier transform spectroscopy techniques). This decision requires a mathematically sound criterion for a satisfactory measurement. Gamry's Single-Sine technique terminates the measurement at each frequency when its signal to noise ratio exceeds a target value.

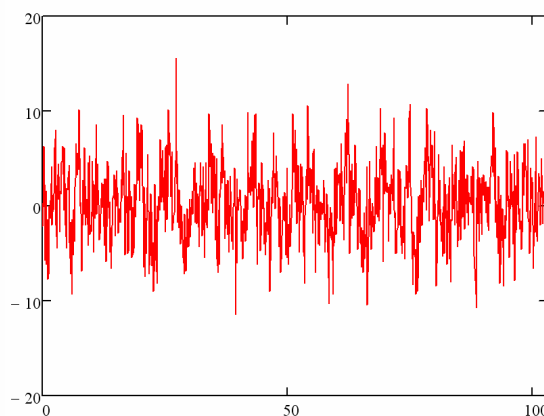
- Phase optimization
 - Pseudo-random phases – watch power spectrum for spikes, phase shift frequencies responsible for spike
 - Repeat

31 frequencies, $A=1$, $\phi=0$



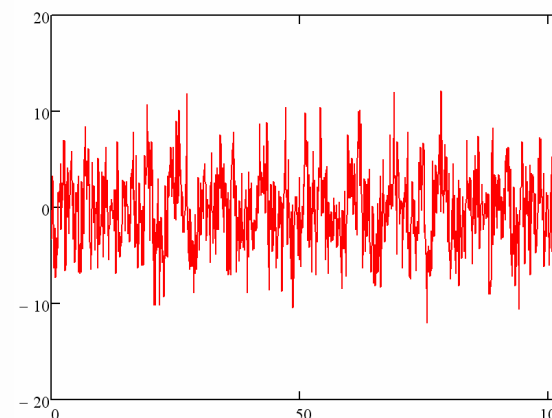
The worst case phase signal vs time.

31 frequencies, $A=1$, $\phi=\text{random}$



The same signal with randomized phases.

31 frequencies, $A=1$, $\phi=\text{pseudo-random}$

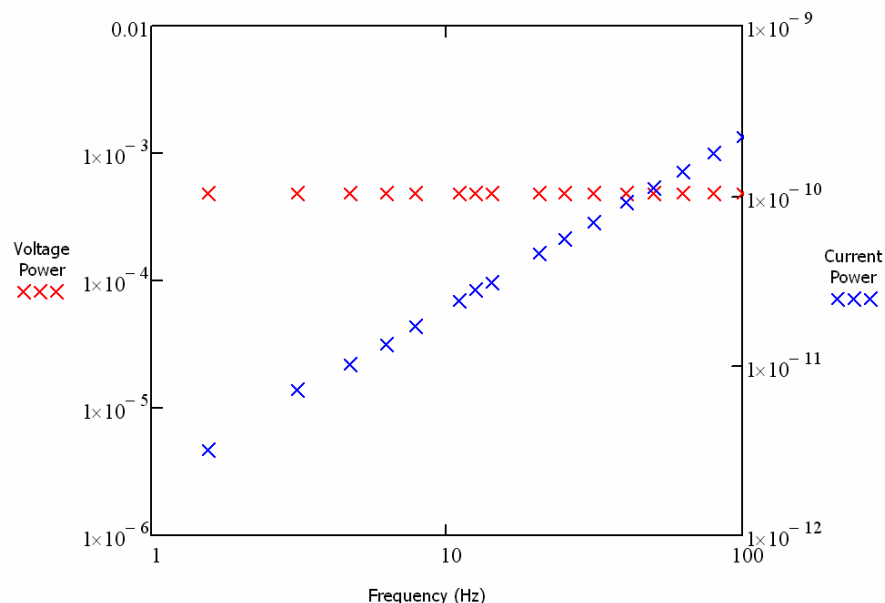


The optimized signal.

OptiEIS™

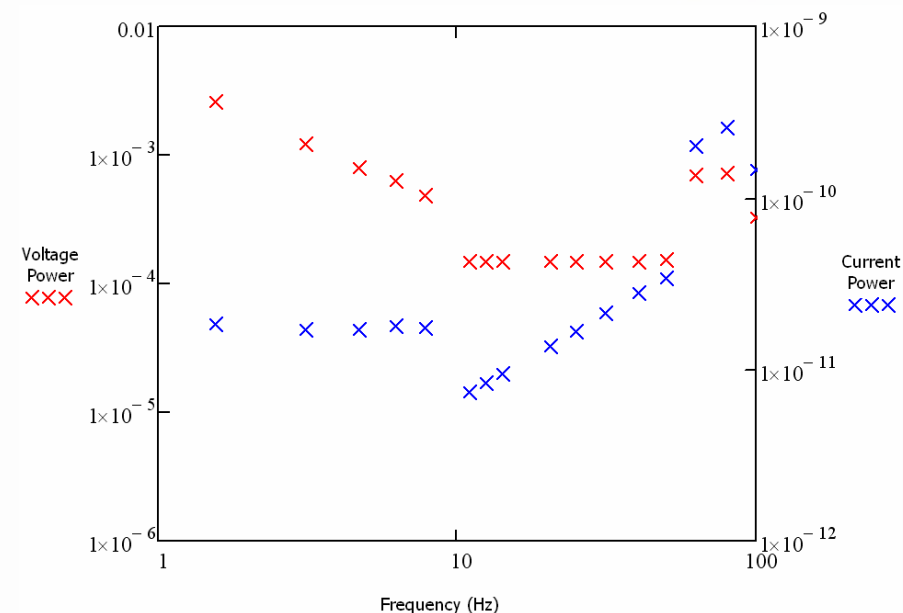
- Amplitude Optimization
 - The measurement at any frequency will converge at different times due to differences in signal to noise (S/N)
 - We can increase the amplitude on the harder (low S/N) frequencies and decrease the amplitude on the easier (high S/N) frequencies to get all frequencies to converge at the same time.

Amplitude Optimization



Fourier transforms of a 1nF capacitor measured using unity amplitude potential signal.

Notice the uniform amplitude on the voltage signal that is used as prepared and the current signal being low at the lower frequencies due to the increase in the impedance of the capacitor.

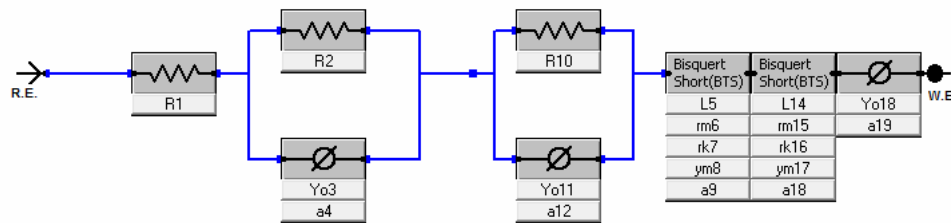


The adjusted applied voltage spectrum and the resulting current spectrum.

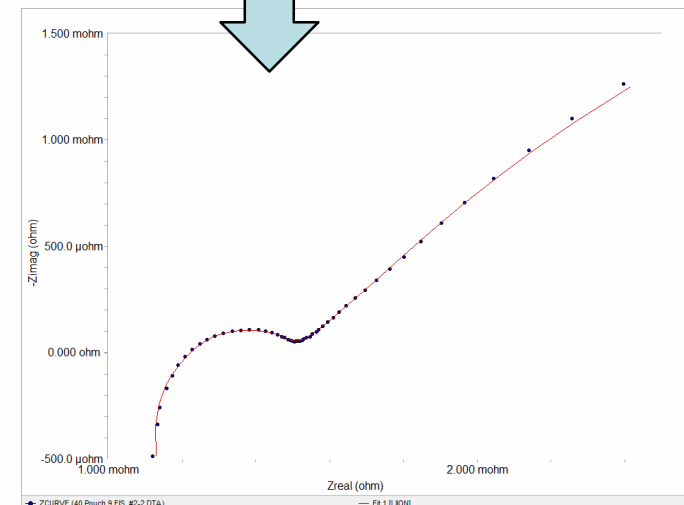
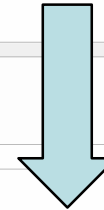
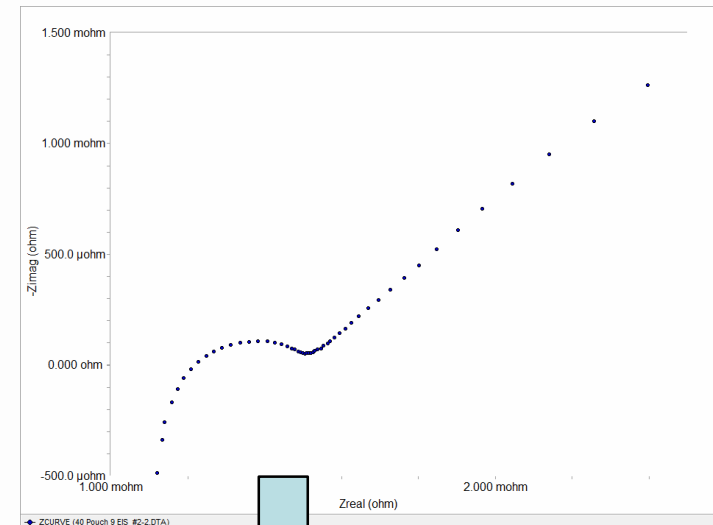
Using a power optimized signal has the effect that all the measurements across the spectrum reach the desired signal to noise level at the same time. This way a significant time savings is achieved.

Autofit

- 15 A-hr Cell

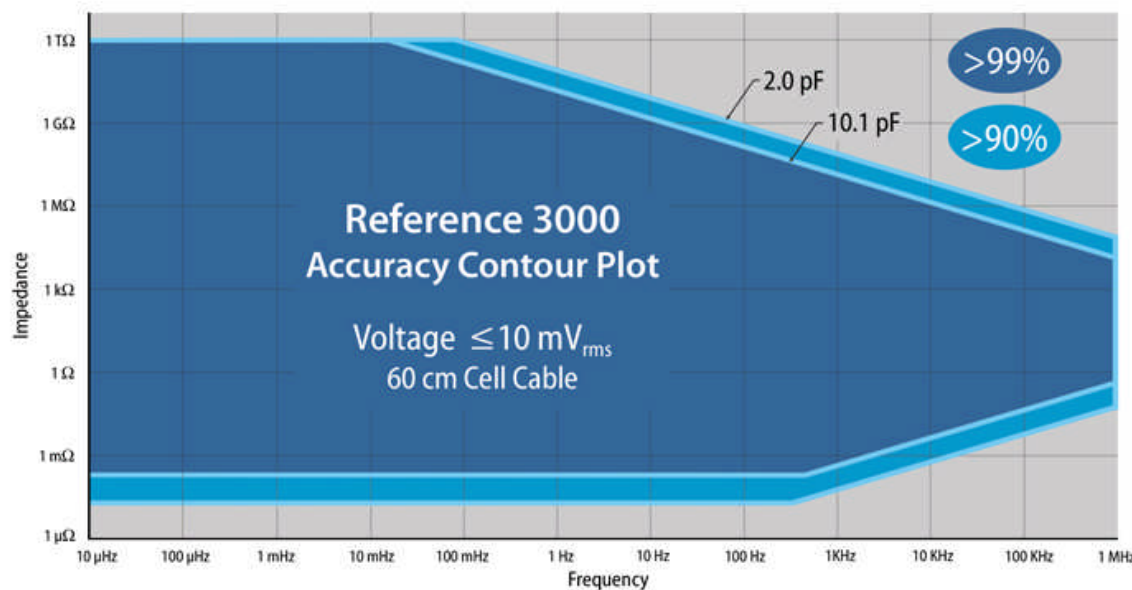


- 17 free parameters (L are locked at 1)
- No knowledge of initial values. All set to 0 except a19



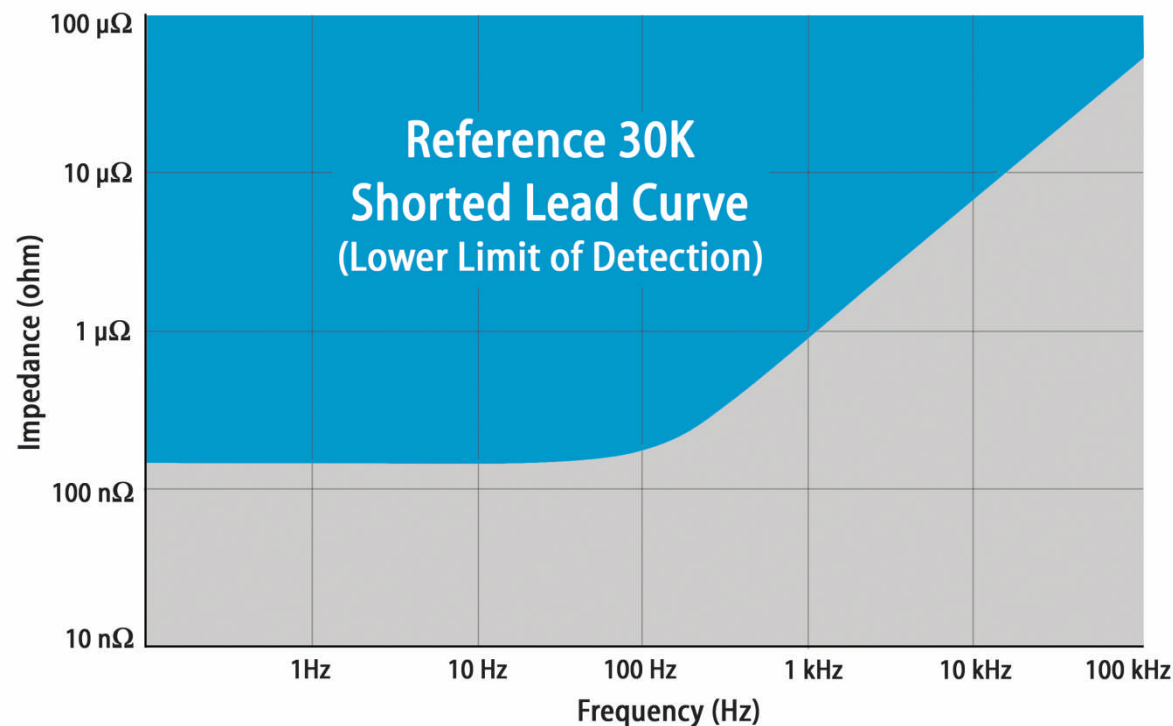
Equipment

- Reference 3000/Reference 3000 Auxiliary Electrometer
 - Up to 1 MHz, Ranges 300 pA – 3 A
 - Impedances less than 500 mΩ at 99% Accuracy
 - Stack impedance (eight channels) up to 100 kHz



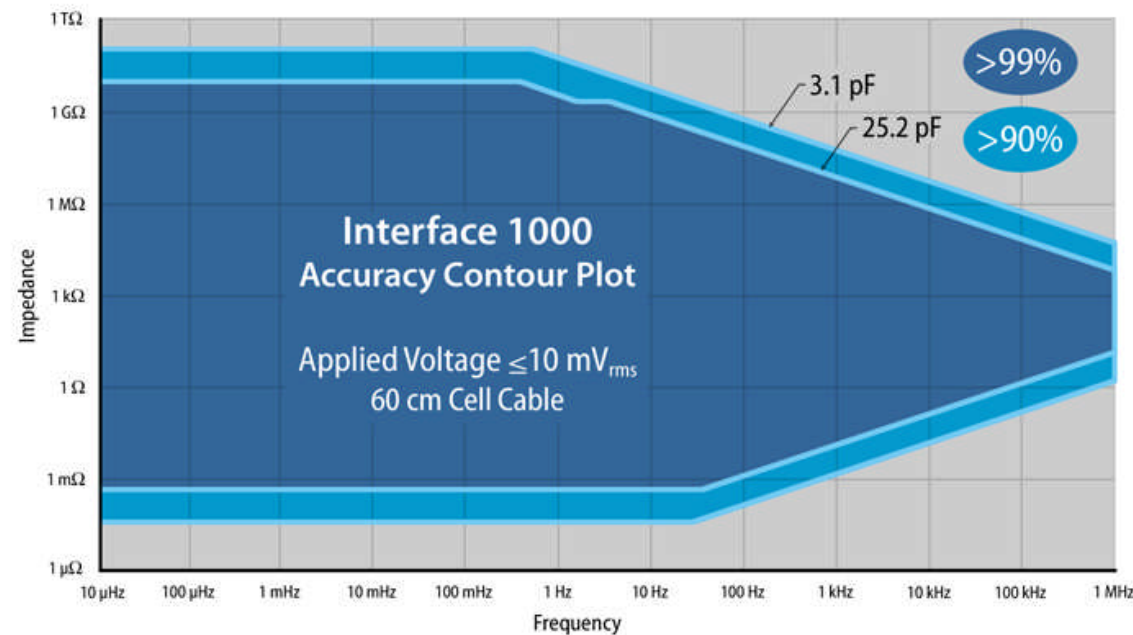
Equipment

- Reference 30K Booster
 - Up to 300 kHz, 30A



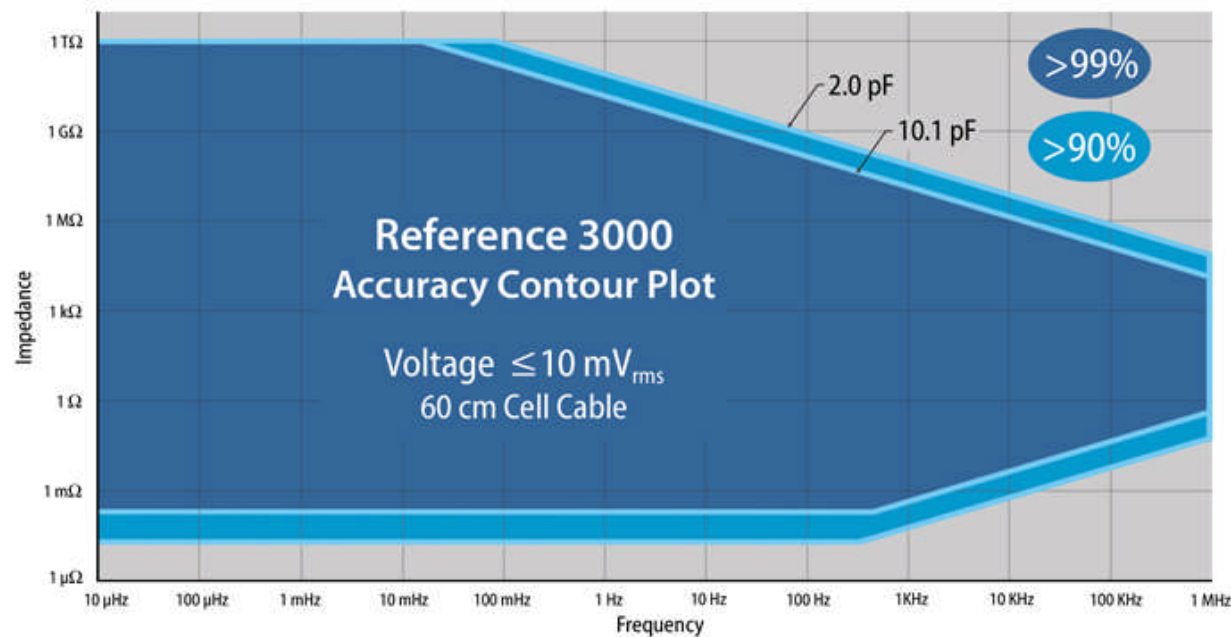
Equipment

- Interface 1000 (single and multichannel)
 - Up to 1 MHz, Ranges 10 nA – 1 A
 - Impedances down to 1 mΩ at 99% Accuracy



Equipment

- Reference 600
 - Up to 1 MHz, Ranges 60 pA – 600 mA



Concluding Remarks

- OptiEIS
 - Phase Optimization
 - Amplitude Optimization
- Autofit
 - No initial guesses needed
- Equipment
 - Potentiostats (single and multichannel) for impedances from $T\Omega$ to $< \mu\Omega$