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A High Measurement Channel Density Impedance Array Analyzer: Instrumentation and Implementation Approaches

Kevin R. Cooper, Matthew Casulli, Matthew Smith and Derek Johnson

Scribner Associates Inc., 150 E. Connecticut Avenue, Southern Pines
North Carolina 28387, USA

The development of impedance-based array devices is hindered by a lack of robust platforms and methods upon which to evaluate and interrogate sensors. One aspect to be addressed is the development of measurement-time efficient techniques for broadband impedance spectroscopy of large electrode arrays. The objective of this work was to substantially increase the throughput capability of low frequency impedance measurement of a large channel-count array analyzer by developing true parallel measurement methods. The goal was achieved by Fourier transform-based analysis of simultaneously-acquired, multi-channel current and voltage data. Efficacy and quantitative analysis of the parallel approach is demonstrated through impedance measurements of dummy cell arrays to sub-Hertz frequencies. Comparison of the accuracy and measurement-time efficiency of the standard-only sequential measurement method and a hybrid high-frequency standard + low frequency parallel approach highlights the efficacy of the latter method when applied to large arrays.

Introduction

There is increasing interest in impedance-based sensors and sensor array systems because the technique can reveal valuable information, including reaction kinetics and charge transfer processes; resistive, capacitive, and dielectric properties of the sensor materials; and transport effects (1,2). The development of impedance-based array devices is hindered in part by a lack of robust platforms and methods upon which to evaluate and interrogate electrode or sensor arrays.

Commercially-available, general purpose multi-channel analyzers capable of DC interrogation of arrays, with up to 100 electrodes, have been used to study complex electrochemical phenomena such as, metallurgical and spatiotemporal interactions in localized corrosion (3-9), for combinatorial electrochemistry for discovery of improved corrosion inhibitors (10,11), lithium-ion battery electrode materials (12-15), and fuel cell catalysts (16). These works employ DC electrochemical measurement methods, such as linear or cyclic polarization techniques. To the authors' knowledge, only one publication (17) describes impedance spectroscopy of large-channel count arrays, *i.e.*, where N ~ 100 electrodes (17).

To date, impedance spectroscopy measurements of arrays have been based on sequential interrogation of each array element at each frequency (17). The advantage of this approach is that only one impedance analyzer is required, substantially reducing the cost, size, mass, and power consumption of the analytical instrumentation. However, a limitation of the serial approach is that the data acquisition time can be substantial at low frequency when interrogating large numbers of array elements, *e.g.* from tens of minutes to tens or even hundreds of hours, when interrogating 100 channels to sub-Hertz frequencies.

There are numerous reasons why time-efficient methods are required for impedance spectroscopy of large electrode arrays. First, there is a need to make the measurement in an experimentally practicable length of time. Second, transient events are more likely to either be missed or misinterpreted if the array is not interrogated with expediency. Finally, applications can be restricted in their power availability and/or are required to function for an extended period of time on a fixed energy budget. Such applications include battery-powered or low-power sourced sensor array systems, as well as systems for space exploration; for these applications, it is highly desirable, if not essential, to minimize the measurement duration. Thus, there is a need to develop time-efficient measurement techniques for broadband impedance spectroscopy for large electrode arrays.

The objective of this work was to substantially increase the throughput capability of low frequency impedance measurement for a large channel count array analyzer by developing true parallel measurement methods. The goal of a true parallel impedance measurement, at frequencies less than ~ 10 Hz, was achieved through development of Fourier Transform based analysis of simultaneously-acquired, time-based, multi-channel current and voltage data. In addition, it was demonstrated that a two-pronged measurement approach consisting of the standard sequential measurement method at high frequencies (*e.g.*, 1 kHz to 10 Hz) combined with the parallel method at low frequencies (*e.g.*, < 10 Hz) was feasible for time-efficient broadband impedance spectroscopy of large arrays. Arrays of resistor-capacitor dummy cells exhibiting frequency-dependent complex impedance characteristics, consistent with chemiresistor and other sensors, were used to demonstrate the efficacy of the approach.

Technique for time-efficient impedance spectroscopy of arrays

The current state-of-the-art array analyzer is the model 910 Multi-channel Microelectrode Analyzer (MMA, Scribner Associates, Inc.). The MMA is a general purpose instrument capable of DC and AC impedance interrogation of arrays with up to 100 electrodes or sensors (17). Impedance spectroscopy measurements with the MMA are based on sequential interrogation of each array element at each frequency. This method is referred to as the "standard" impedance measurement approach. The advantage of the standard approach is that only one impedance analyzer is required, which substantially reduces the cost, size, mass, and power demand of the instrument.

However, the limitation of the standard approach is that at low frequency (less than ~ 1 Hz), the data acquisition time can be substantial when interrogating large numbers of array elements (tens of minutes to tens of hours). As an example, it takes 100 seconds *per electrode* to perform an impedance measurement at 10 mHz, assuming one integration cycle (more integration cycles leads to improved signal-to-noise ratio, at the cost of increased data acquisition time). An impedance measurement at this frequency performed sequentially on a 100-electrode array takes 2.8 hours. This example demonstrates that non-parallel approaches to impedance measurement of large-channel count arrays leads to lengthy data acquisition times at low frequencies.

It is obvious, from the results shown in Table 1, that there are substantial gains in measurement time efficiency through implementation of a true parallel measurement approach for large electrode arrays. The benefit afforded by the parallel method increases substantially as the minimum frequency decreases; as the minimum AC frequency decreases (sub-Hertz), the measurement time grows exponentially for the standard method, whereas it increases nearly linearly for the parallel method. As demonstrated by the results in Table 1, to be time-efficient, low-frequency impedance measurements of arrays must be performed in parallel. Therefore, the objective of this work was to develop a practicable multi-channel impedance measurement method.

Table 1. Time required to measure the impedance of 100 electrodes *vs.* the minimum frequency using two approaches. In all cases the maximum (initial) frequency was 10^6 Hz.

Minimum (Final) Frequency	*10 Hz*	*1.0 Hz*	*0.1 Hz*	*0.01 Hz*
	Measurement time, min			
Standard Method Only	26	46	264	2452
Standard Method + Parallel Method	26	29	33	55
Time Reduction Factor	1.0x	1.6x	8x	45x

To achieve this, we developed a Fast Fourier Transform (FFT) based method (18,19). The method is described in detail in ref. (20). The FFT approach uses nearly simultaneously-acquired, time-domain, current and voltage data permitting true parallel impedance analysis of multi-electrode arrays. In this method, a common AC voltage excitation of known magnitude and frequency is imposed simultaneously on each element in the array for which an impedance measurement will be made. The current response from each sensor and the voltage are acquired in real-time. Fourier transform of the time-based voltage and current signals into the frequency domain recovers the original frequency-dependent applied AC voltage, and AC current response, of each channel, which are subsequently used to calculate the complex impedance of each electrode within the array.

To examine the efficacy of the parallel low frequency approach to impedance spectroscopy of large channel sensor or electrode arrays, impedance scans of a larger array of simple circuits, comprised of a resistor in series with a capacitor and resistor parallel combination (R_s-$R_p||C_p$), were conducted. An objective of this work was to determine system performance empirically.

The impedance spectra of the R_s-$R_p||C_p$ circuits were measured with two different approaches. In the "standard" method, the impedance measurement is based on sequential interrogation of each array element at each frequency (17). The impedance of each array element, at that frequency, is determined by the single-channel frequency response analyzer. The parallel approach relies on Fourier transform-based analysis of simultaneously-acquired, time-based, multi-channel current and voltage data. In addition, we demonstrate a two-pronged measurement approach consisting of the standard sequential measurement method at high frequencies (10 kHz to 1 Hz) combined with the parallel method at low frequencies (1 Hz to 1 mHz). The benefit of the parallel method, described previously, is a significant reduction in measurement time in comparison to the sequential, or standard, approach.

The goal is to compare the methods to determine which method is faster, and whether one method yields more accurate data. With this information, it will be possible to conduct an exercise in measurement economics; that is, a cost-benefit analysis with respect to measurement time and accuracy.

Experimental

Instrumentation

All experimental work was performed using a using a commercially available PC-controlled Multi-channel Microelectrode Analyzer, MMA (Model 910, Scribner Associates, Inc.). Details of the experimental set-up are described in (20). For all parallel type tests described below, all 100 channels of the MMA were monitored while the AC signal was applied to the array. Time-stamped, multi-channel current and single-channel voltage data were acquired at a rate of ~ 22 frames/second. That is, the current from each of the 100 channels and the common voltage signal were sampled more than 20 times per second.

Testing and evaluation of parallel and time-efficient impedance measurement methods

Because the focus of this work is evaluation of the performance of the analytical instrumentation and developed measurement techniques, testing was conducted using arrays of dummy cells composed of electrical components (resistors and capacitors) giving the advantage that the impedance of the circuit is known. Therefore, the performance of the analytical instrument and measurement methods can be accurately judged.

Circuits composed of resistors and capacitors were used to evaluate the impedance measurement of test elements with frequency-dependent complex impedance values consistent with typical chemiresistor sensors (21-26). The circuit chosen for this work consisted of a resistor (R_s) in series with a parallel resistor-capacitor element ($R_p||C_p$); such an equivalent circuit is commonly used to represent an electrochemical half-cell with a single time constant and negligible mass transport resistance (19). Component values are shown in Table 2. Duplicates of each R-C circuit type were tested.

The R-C array, the standard impedance scan consisted of a 10 mV AC perturbation, applied over a minimum of four integration cycles, through the frequency range of 10 kHz to 1 mHz. No DC bias was applied to the dummy cell. For the second impedance scan, a combination of the parallel method and standard method was used. The full frequency range was partitioned in to a high and low frequency portion. The standard impedance measurement method was used (same conditions as above) for the high frequency segment, 10 kHz to 1 Hz. The parallel method was used for the low frequency segment (1 Hz to 1 mHz) with a 50 mV AC perturbation, for a minimum of 4 cycles. Data was acquired on all 100 channels simultaneously at a rate of approximately 22 frames/sec (~ 2,200 samples/sec).

The resulting impedance spectra were analyzed in ZView™ (Scribner Associates) to perform an iterative least squares fitting method to determine component values. The fitted R_s, R_p, and C_p values were compared between both experimental methods to determine whether there was an appreciable difference in measurement performance. Additionally, the experiment duration for the standard only and the hybrid standard + parallel method were evaluated to determine the trade-off economics of each measurement method.

Table 2. Nominal values of resistor and capacitor components used in the dummy cell circuits used in this work. R_s = series resistor, R_p = parallel resistor, C_p = parallel capacitor.

Dummy Cell	*Nominal Values*		
Type	*R_s, kΩ*	*R_p, MΩ*	*C_p, μF*
A			0.1
B	1.0 (±1%)	0.1 (±2%)	8
C			74
D			0.1
E	1.0 (±1%)	1 (±2%)	8
F			74

Results and Discussion

The results of experiments designed to demonstrate the efficacy of a combined sequential (standard) + parallel measurement approach on dummy cells composed of resistor-capacitor networks that mimic typical sensor and/or electrochemical systems in their frequency-dependent impedance response are described.

The performance of a multi-channel impedance analyzer was assessed using an array of dummy cells that exhibit frequency-dependent response and with impedance and reactance values consistent with typical chemiresistor sensors (21-26) Dummy cells composed of electrical components (resistors and capacitors) have the advantage that the frequency-dependent impedance of the circuit is known *a priori*, and therefore, can accurately judge the performance of the analytical instrument.

As indicated in the experimental section, two types of impedance experiments were conducted: the standard sequential measurement approach and the combined or hybrid standard + parallel low frequency approach described in detail elsewhere (20).

Impedance spectra for the 6 dummy cell types (Table 2) are shown in Figure 1. In each case, the results for the full standard method and the hybrid standard + parallel method are shown. The predicted impedance response based on the nominal values for the components is also shown. In general, the plots in Figure 1 indicate that the new hybrid approach is just as accurate as the standard method. The most obvious difference is the presence of high frequency inductive behavior in the actual measurements which was not accounted for in the equivalent circuit modeling.

Table 3 summarizes the results of the impedance experiments on the dummy cell array. The average obtained from each pair of nominally identical dummy cells is shown. In general, both measurement methods provided accurate results. Specifically, with one exception noted below, the difference (or error) between the predicted value of the dummy circuit components, obtained from a fit of the measured spectra to an equivalent circuit model, and the nominal values were less than ~ ±2.5%.

A significantly larger error (~ 13%) was observed for the predicted value of the series resistance for Type A and D dummy cells (nominal R_s = 1 kΩ, C_p = 0.1 μF). Series inductance can have the effect of increasing the apparent series resistance. However, accounting for the high frequency inductance in the data only decreased the error in the fitted R_s value to ~ 10%. Thus, although accounting for inductance improved the accuracy of the fit result for the series resistance, it does appear to the dominant source of the error. This measurement error was noted in separate experiments that are not described in detail here. The error was observed only when the dummy cell includes a parallel resistor-capacitor element ($R_p||C_p$). That is, this error is not evident when measuring a resistor alone. Furthermore, the error only manifested itself when the series resistance R_s was 1 kΩ and the parallel capacitance was 0.1 μF. Additional tests not detailed here indicated that a capacitive element of 0.1 μF coupled with higher series resistance (*e.g.*, 1 MΩ) did not result in a significant error in the measured series resistance. Identification of the source of the error is on-going.

Table 4 compares the difference in the measurement error percent for the two methods. The results indicate there was little difference in the data yielded by the two methods. That is, both methods results in comparable values and neither method consistently gave more or less accurate results.

That comparable results were obtained by the two methods is further observed in Figure 2 wherein the datasets overlap to the point that they are difficult to distinguish graphically. Figure 2 provides examples of the high and low frequency data for a Type C and Type A dummy cell, respectively. The 1 Hz transition frequency (from standard to parallel measurement method) is labeled. Some additional noise is evident in the data obtained using the parallel approach, but overall these representative data illustrate that the difference in the measured impedance, is minimal.

Comparable accuracies provide the luxury of using the time savings to determine which measurement approach is preferred for a given test scenario. When the time required to perform the impedance spectra for the array is considered, the efficacy of the hybrid standard + parallel method can achieve up to a 100-fold reduction in measurement time, in comparison to the standard technique alone.

Table 3. Dummy circuit component values from equivalent circuit model fit of impedance spectra obtained using the standard-only and hybrid standard + parallel approaches. Results are the average of two nominally identical dummy cells for each type. Standard method: 10 mV_{AC}, 10 kHz to 1 mHz. Standard + Parallel method: Standard portion 10 mV_{AC}, 10 kHz – 1 Hz, Parallel portion: 50 mV_{AC}, 1 Hz – 1 mHz. 10 points/decade for all cases.

Type		*Nominal*	*Standard*		*Standard + Parallel*	
			Fit Result	*Difference from Nominal*	*Fit Result*	*Difference from Nominal*
A	R_s, kΩ	1.00 ± 1%	1.13	13.3%	1.13	13.4%
	R_p, kΩ	100 ± 2%	99.4	-0.6%	99.4	-0.6%
	C_p, μF	0.1	0.102	2.1%	0.102	2.3%
B	R_s, kΩ	1.00 ± 1%	1.02	2.0%	1.02	2.1%
	R_p, kΩ	100 ± 2%	98.5	1.5%	98.7	-1.3%
	C_p, μF	8	8.10	1.2%	8.14	1.8%
C	R_s, kΩ	1.00 ± 1%	1.01	1.3%	1.01	1.4%
	R_p, kΩ	100 ± 2%	98.0	2.0%	98.1	-1.9%
	C_p, μF	74	73.1	-1.2%	73.0	-1.3%
D	R_s, kΩ	1.00 ± 1%	1.13	13.1%	1.13	13.0%
	R_p, MΩ	1.00 ± 2%	0.998	-0.2%	0.978	-2.2%
	C_p, μF	0.1	0.102	2.3%	0.102	2.4%
E	R_s, kΩ	1.00 ± 1%	1.02	2.1%	1.02	2.2%
	R_p, MΩ	1.00 ± 2%	0.988	-1.2%	0.973	-2.7%
	C_p, μF	8	8.10	1.3%	8.23	2.9%
F	R_s, kΩ	1.00 ± 1%	1.01	1.2%	1.01	1.3%
	R_p, MΩ	1.00 ± 2%	0.964	-3.6%	0.960	-4.0%
	C_p, μF	74	73.4	-0.8%	75.6	2.1%

For example, for the tests conducted in this work, 100 channels were measured via the parallel method in 0.233 days. In contrast, measurement of just 24 channels via the standard method over the full frequency range took 5.6 days to complete. Had the standard method been applied to the full 100-channel array, it would have taken 23.3 days to complete. Thus, a 100-fold reduction in measurement time was achieved using the new, hybrid impedance measurement method. The significant improvement in measurement time efficiency was attained with no loss in measurement accuracy, thus demonstrating the efficacy of the approach to high-throughput low frequency impedance of large electrode arrays. These results clearly demonstrate that true parallel approaches are required for practical impedance spectroscopy of a large numbers of electrodes.

Table 4. Difference in the percent deviation of the measured value *vs.* the nominal component value between the two methods, $\varepsilon_{standard} - \varepsilon_{hybrid}$, where ε is the % deviation of the measured value from the nominal component value. The difference in deviation from the nominal for the two methods was generally less than ±2%, *i.e.*, $|\varepsilon_{standard} - \varepsilon_{hybrid}| < 2\%$.

Type	R_s	R_p	C_p
A	0.00%	0.01%	-0.21%
A	-0.20%	-0.05%	-0.16%
B	-0.10%	0.18%	-0.59%
B	0.00%	0.23%	-0.58%
C	0.00%	0.07%	-1.99%
C	-0.20%	0.07%	-3.32%
D	0.00%	-1.88%	0.24%
D	0.20%	-2.09%	-0.39%
E	0.00%	-1.49%	-1.50%
E	-0.10%	-1.67%	-1.72%
F	-0.10%	-0.05%	-1.21%
F	0.00%	-0.84%	-0.79%

Conclusions

This work demonstrates the technical feasibility of implementing an enhanced, time-efficient approach to low frequency impedance measurement of large channel-count electrodes and sensor arrays. The method is based on Fourier analysis of multi-channel current and voltage data acquired in real-time, and is truly parallel in nature. Dummy cells representative of a simple electrochemical cell or sensor were used to probe the efficacy of the parallel measurement approach to impedance measurement. The results demonstrated that the array analyzer, and either the standard or the parallel measurement approach, were capable of accurately determining the impedance of the investigated dummy cells. When the impedance of the array was measured from 10 kHz to 1 mHz, the measurement time was two orders of magnitude shorter for the hybrid standard + parallel method in comparison to the standard sequential method alone. Furthermore, the substantial improvement in measurement time efficiency was achieved without sacrificing measurement accuracy.

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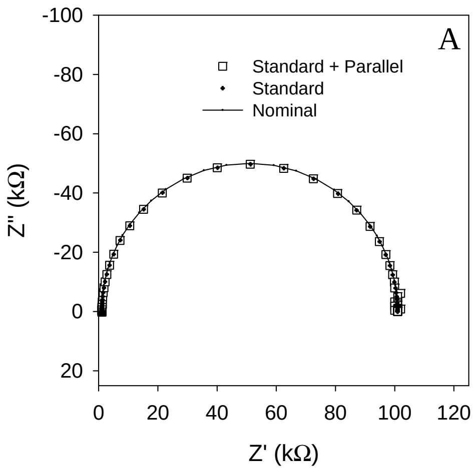
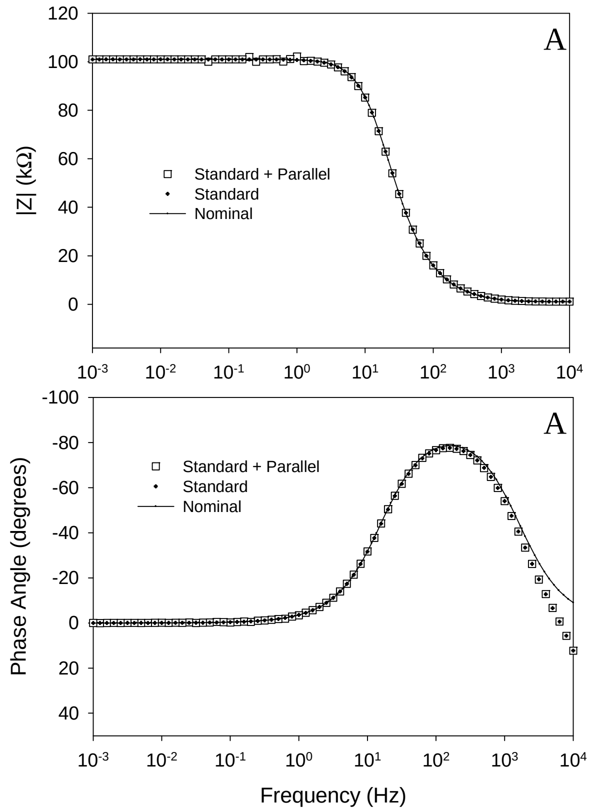
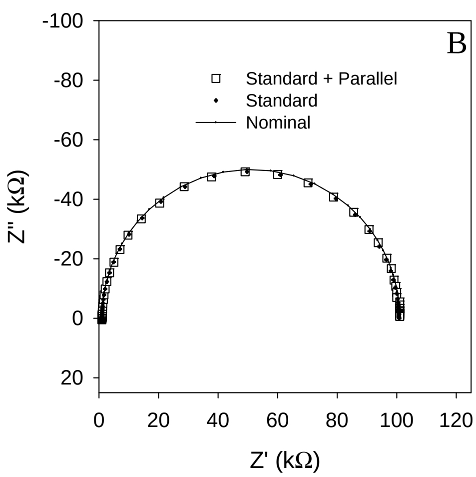
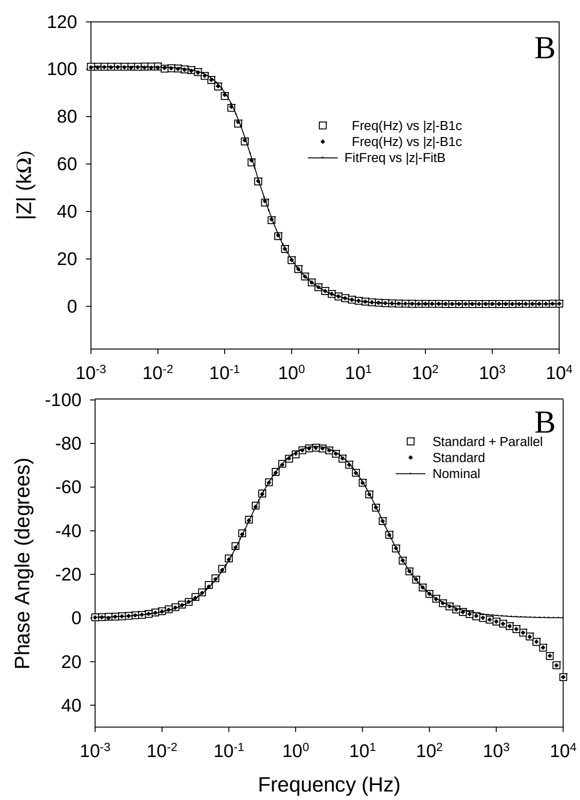




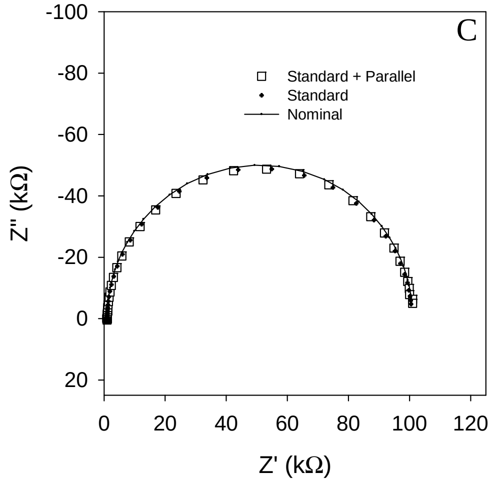
Type A
$R_s = 1\ k\Omega$
$R_p = 100\ k\Omega$
$C_p = 0.1\ \mu F$

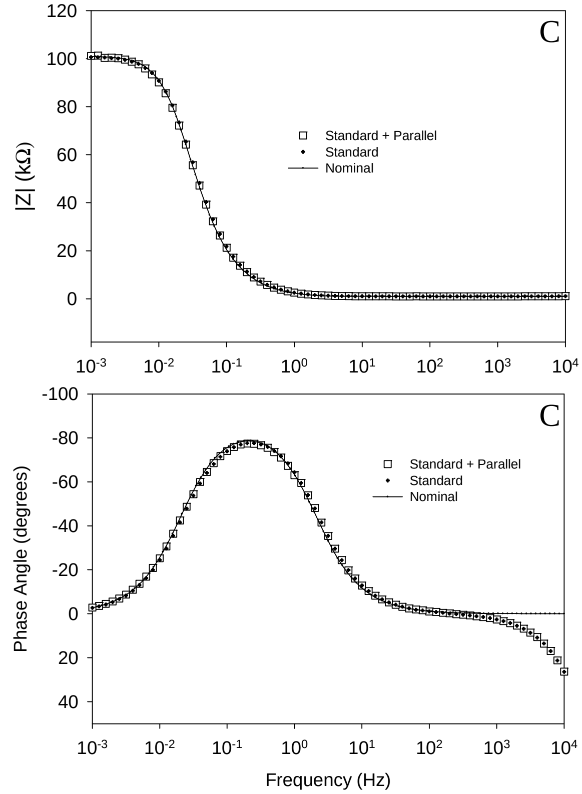




Type B
$R_s = 1\ k\Omega$
$R_p = 100\ k\Omega$
$C_p = 8\ \mu F$

Figure 1. Complex plane plots and Bode plots of simple R_s-$R_p||C_p$ dummy circuits composed of different component values. The results for Types A and B are shown above, and Types C through F are shown on the following pages.



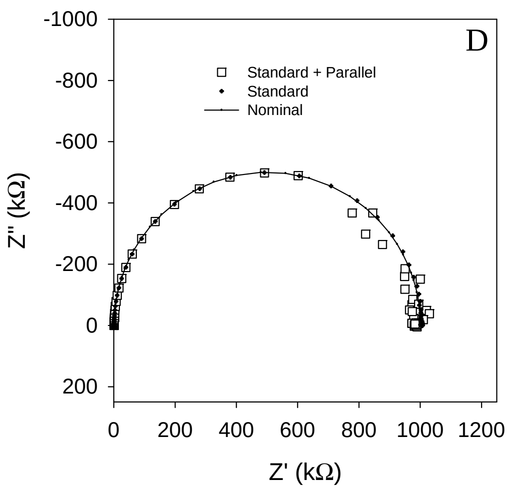


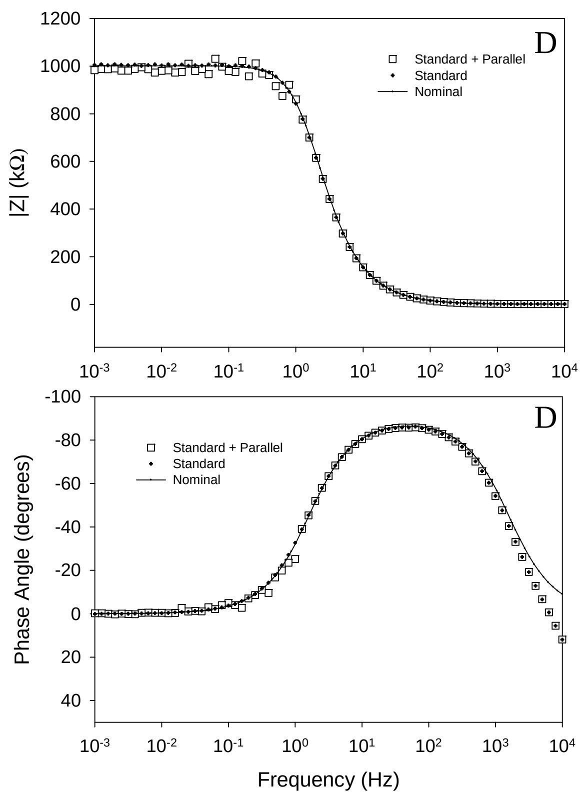
Type C

$R_s = 1\ k\Omega$

$R_p = 100\ k\Omega$

$C_p = 77\ \mu F$



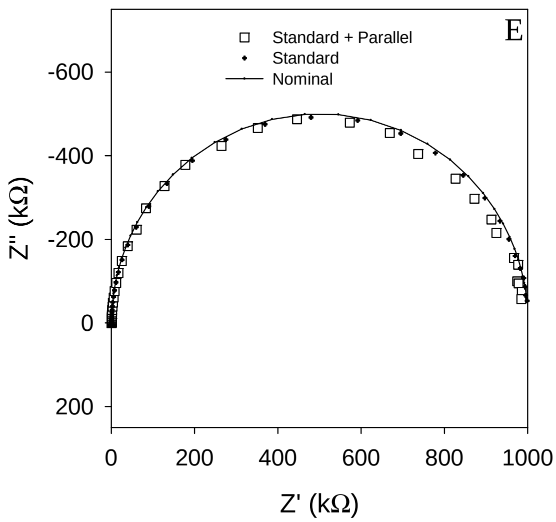


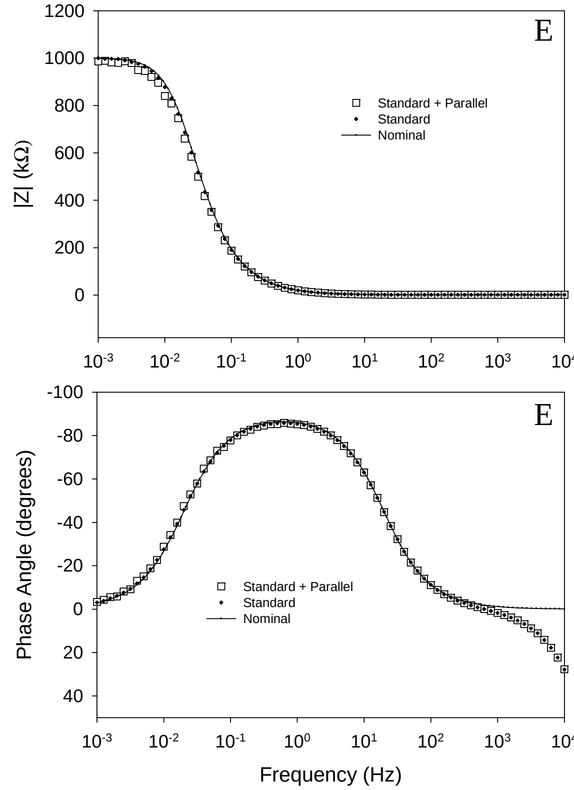
Type D

$R_s = 1\ k\Omega$

$R_p = 1\ M\Omega$

$C_p = 0.1\ \mu F$



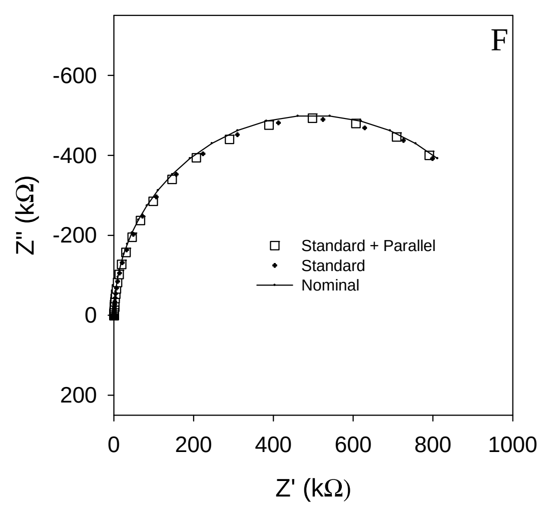


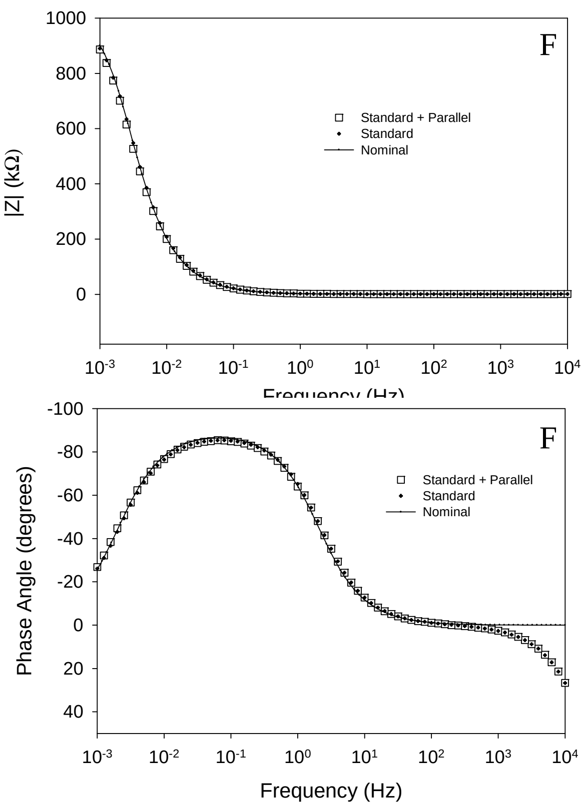
Type E

$R_s = 1$ kΩ

$R_p = 1$ MΩ

$C_p \sim 8$ μF



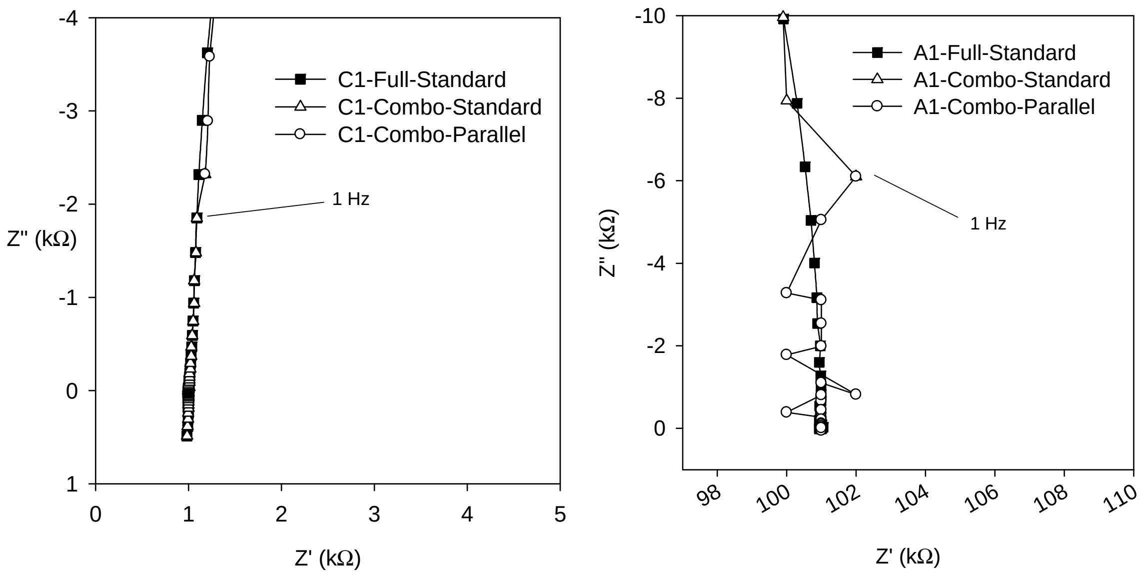


Type F

$R_s = 1$ kΩ

$R_p = 1$ MΩ

$C_p \sim 77$ μF



(a) (b)

Figure 2. (a) High frequency potion of a Type C circuit. At 1 Hz the combination scan transitions between parallel and standard methods. (b) The low frequency portion of a Nyquist plot of a Type A circuit. A greater level of noise is evident in the data acquired using the parallel method in comparison to the standard, sequential method. In both plots, for the combined standard + parallel approach, the transition frequency was 1 Hz.