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# Ohmic Drop Compensation in Voltammetry: Iterative Correction of the Applied Potential

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# Ohmic Drop Compensation in Voltammetry: Iterative Correction of the Applied Potential

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## Abstract

A new method of ohmic potential-drop correction for use with potential step and sweep voltammetric methods is described. The method, Iterative Correction of the Applied Potential, ICAP, essentially replaces an electronic positive feedback correction with a digital positive feedback correction. This paper will present one form of the ICAP procedure in which voltammetric current data acquired by a high-speed digital oscilloscope is used to iteratively generate a compensating potential waveform that is then synthesized by an arbitrary waveform generator. The ICAP method is advantageous for high-speed measurements since many of the difficulties caused by electronic positive-feedback compensation are eliminated.

## Introduction

Ohmic potential drop (iR drop), caused by flow of current through the cell solution resistance, is an inescapable consequence of voltammetric measurements. Development of methods for compensation of the effect of ohmic potential drop has its roots in the earliest developments of modern potentiostatic circuits[1-3]. Two of the most widely used methods are electronic positive-feedback and current-interuption compensation. The current-interruption method corrects for iR drop by periodically interupting the current through the electrochemical cell. The working electrode potential is measured during the current interuption and hence correction can be made during conditions of zero iR drop[4]. A difficulty with the current-interruption method is that the interuption process limits the measurement bandwidth to a few kilohertz[1], which confines the technique's usefulness to low-frequency work.

Electronic positive-feedback compensation works with a positive feedback loop. A correction voltage signal proportional to the instantaneous current through the electrochemical cell is summed with the applied excitation potential. For low-frequency work, the feedback loop can quite accurately correct a large fraction of the ohmic potential drop. At higher frequencies, the feedback loop must be carefully designed to avoid delaying the compensation signal. Amatore and Lefrou have recently reported on an instrument useful for cyclic voltammetric scans as rapid as 500,000 V s$^{-1}$[5]. However, it is clear from Amatore and Lefrou's work and from others[1, 2, 6, 7] that quite careful design and implementation of the positive feedback loop is required to make fast voltammetric measurements and to avoid introducing additional distortion. A major cause of difficulty is that the compensating signal is delayed by passage through the several amplifiers required to implement the positive feedback loop. This causes the compensation signal to be increasingly in error as the measurement time scale becomes smaller.

In this paper, a method of ohmic potential drop compensation that uses a digital positive-feedback loop is demonstrated that may be more appropriate for use with high-speed voltammetry. In addition, the digital feedback loop can also be used with existing instrumentation that do not currently have provision for electronic ohmic potential drop compensation. Because the electronic positive feedback loop is not required, most of the difficulty in construction and analysis of potentiostatic circuitry is eliminated. Instead the digital feedback loop digitizes the current signal and sums it with the excitation potential (e.g. the triangle wave in cyclic voltammetry). The resulting waveform is loaded into an arbitrary waveform

generator and is used as the new excitation waveform. By iteratively performing this process it is possible

to develop a waveform that can compensate for the ohmic drop in solution. This process is referred to as

the Iterative Correction of the Applied Potential (ICAP) method. The digital feedback loop (that is the

digitizer and arbitrary waveform generator) of the ICAP method can outperform a direct electronic loop in

the sense that problems due to signal delay in the compensation loop are removed from the circuit. This is

because even moderate-performance digital oscilloscopes used as a digitizer can have analog bandwidths in

excess of 20 MHz. This bandwidth is difficult to achieve in a conventional electronic feedback loop. Also,

any residual delay in the digital loop can be easily compensated for after the digitization step.

This paper describes an implementation of the ICAP method and demonstrates ohmic drop

compensation for cyclic voltammetry of ferrocene in acetonitrile and tetrahydrofuran solvents.


## Experimental

**Reagents:**  Ferrocene (Strem Chemicals, Newburyport, MA) was purified by sublimation.

Tetrabutylammonium fluorophosphate (TBAPF$_6$, electrometric grade, SACHEM, Austin, TX),

tetrahydrofuran (THF, HPLC grade, J. T. Baker, Phillipsburg, NJ), and acetontrile (HPLC grade, Fisher

Scientific, Fair Lawn, NJ) were used as received.

**Electrodes:**  The gold microdisk electrode used in this experiment was prepared according to

published methods(8). The electrode has a radius of 52 μm(9) and is sealed in glass. The electrode was

polished with 0.05 μm alumina slurry on a cloth pad, rinsed with a stream of distilled-deionized water, and

pure solvent prior to collecting voltammograms. A silver wire served as a quasi-reference electrode and a

platinum wire was the auxiliary electrode. Under the conditions reported here (v ≥ 50 V/s), all

voltammograms can be considered to occur under linear diffusion conditions(10).

**Instrumentation:**  All measurements used a three-electrode potentiostat, constructed in-house. At the

gain used in these experiments the current amplifier has a small-signal rise time of 1.5 μs. However, due to

slew-rate limitations, the maximum undistorted scan rate available with this instrument was about 2000

V/s.

Voltammetric data were acquired on a Tektronix model TDS 540A digitizing oscilloscope (Tektronix,

Beaverton, OR) with a maximum digitization rate of 1 GS/s. Potential waveforms were generated by a

Wavetek model 395 arbitrary waveform generator(Wavetek, San Diego, CA). The arbitrary waveform generator has a maximum output rate of 100 MS/s with a record length of up to 64k points. A '486 level personal computer was used to store data, calculate new potential waveforms, download data from the oscilloscope, and upload potential waveforms to the arbitrary waveform generator. A IEE-488 GPIB bus interface card (CIO-PC2A, Computer Boards, Inc., Mansfield MA) was used for data transfer between the computer, oscilloscope, and waveform generator.

Impedance data were acquired with the use of a dual-phase digital lock-in amplifier (Model 850 Stanford Research Systems, Sunnyvale CA). Data were acquired as phase and magnitude for frequency sweeps from 0.100 to 100 kHz. The excitation waveform was a 100 mV rms sine wave generated by the lock-in amplifier's internal generator. The ac waveform was applied directly across a silver counter electrode and the working electrode. Cell currents were measured as the voltage drop across a 10 $\Omega$ resistor. Impedance-frequency curves were fit to an electrical model with the use of Sigma-Plot (version 2.0, Jandel Scientific, San Rafael CA).

The digital simulation program for cyclic voltammetry with ohmic drop has been described in a previous paper(11).

**Computer Methods**  The iterative correction method was implemented in a computer program written in the C language (Visual C++, Version 1.5, Microsoft, Redmond WA) running under MS-DOS. The program includes routines to download data from the oscilloscope over the GPIB bus, graphically present the data, and store the data on disk. In addition, the program allows the user to generate an arbitrary sequence of potential sweeps and steps by uploading the desired waveform to the arbitrary waveform generator, AWG. The potential resolution of the AWG is 12 bits but the output is scaled to provide the highest resolution, so that a 2 volt scan has a minimum step size of $< 0.5$ mV. The software and hardware described here are adequate for generating precise, accurate sweeps from much less than 1 mV/s to as large as $10^6$ V/s.

The software described also performs the iterative correction of the applied potential (ICAP) method. A general outline of the steps required for the method are described below:  (a) The desired voltage waveform to be applied is generated according to user input. (b) Upon the user request, the program converts the potential waveform to a stream of data points and uploads the waveform to the computer. The

waveform generator is programmed to emit the waveform and simultaneously trigger the oscilloscope. (c) The acquired current *and* potential waveform are then automatically downloaded from the oscilloscope and saved to disk. Once the initial current-potential data, generation 0, are saved, the ICAP method can proceed. The generation 0 current trace is multiplied by the desired amount of compensation resistance and is added to the generation 0 potential trace to give a first-order correction potential waveform. (d) This corrected waveform is converted to the format required by the waveform generator and, upon user request, the corrected waveform is emitted. (e) The generation 1 current-potential data are then downloaded from the oscilloscope. (f) The generation 1 current is multiplied by the compensation resistance and is applied to the generation 0 potential waveform to give a second-order correction. At this point the procedure is repeated from step (d) until the current-potential curves converge (i.e. remain the same from generation to generation). Convergence typically takes from 5 to 15 generations depending on the amount of ohmic drop. For the results reported here, convergence was noted by the experimenter. Future implementations of the method will likely automate the convergence detection. Note that the final resulting current waveform is always plotted versus the generation 0 potential waveform.

A copy of the program implementing the ICAP method is available upon request.

## Results and Discussion

**ICAP Corrected Voltammetry**  The ICAP method is shown in Figure 1 as applied to a dummy cell consisting of a 100 kΩ resistor in series with a 10.5 nF capacitor. The figure shows the initial scan and successive scans upon applying the iterative correction for 10 generations. Figure 1a shows the result of a correction at 90 % of the total resistance and Figure 1b at 100 %. At 100 % correction a large amount of overshoot and the beginning of sustained oscillations ("ringing") is observed. Additional iterations at the 100 % or greater level cause a continued increase in the amount of overshoot and ringing. At the 90% level there is some overshoot and ringing but, in contrast to greater compensation levels, the overshoot does not increase with additional iterations.

A comparison of the 0 and 90% compensation (after 10 generations) applied to the dummy cell and to a  dummy cell with 0 Ω resistance is shown for comparison in Figure 2. Note that the overshoot is about 12-15% of the total charging current. The overshoot can be further reduced by performing additional

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iterations but the minimum overshoot is still about 10 %. Lower levels of compensation will further reduce the amount of overshoot.
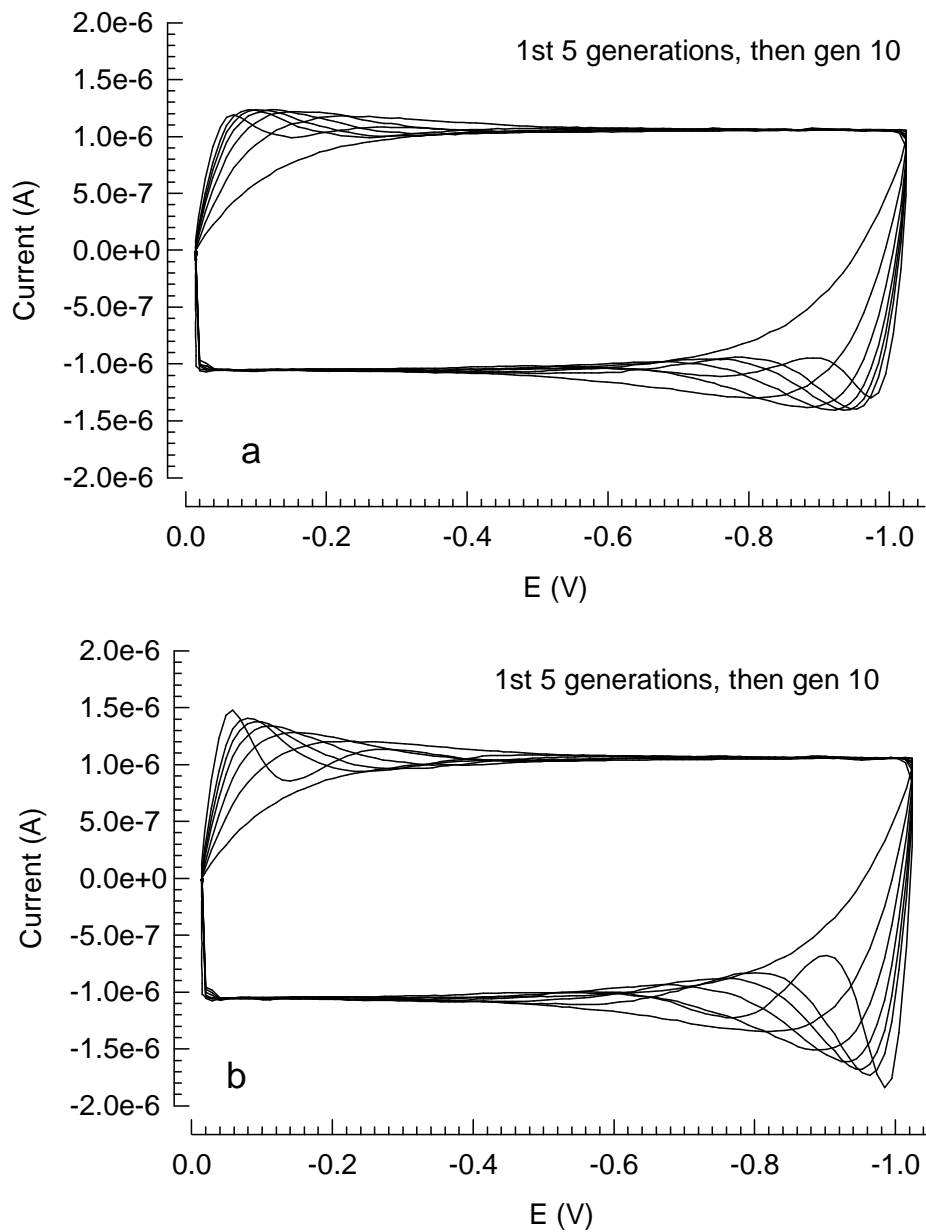


**Figure 1.** ICAP correction applied to cyclic voltage sweep applied to a dummy cell. Shown are the first 5 generations and then generation 10. Voltage sweep rate is 100 V/s. Dummy cell is a series resistor (100 kΩ) and capacitor (10.5 nF) in combination. (a.) Compensation at 90 kΩ (90%) level. (b.) Compensation at 100 kΩ (100%) level
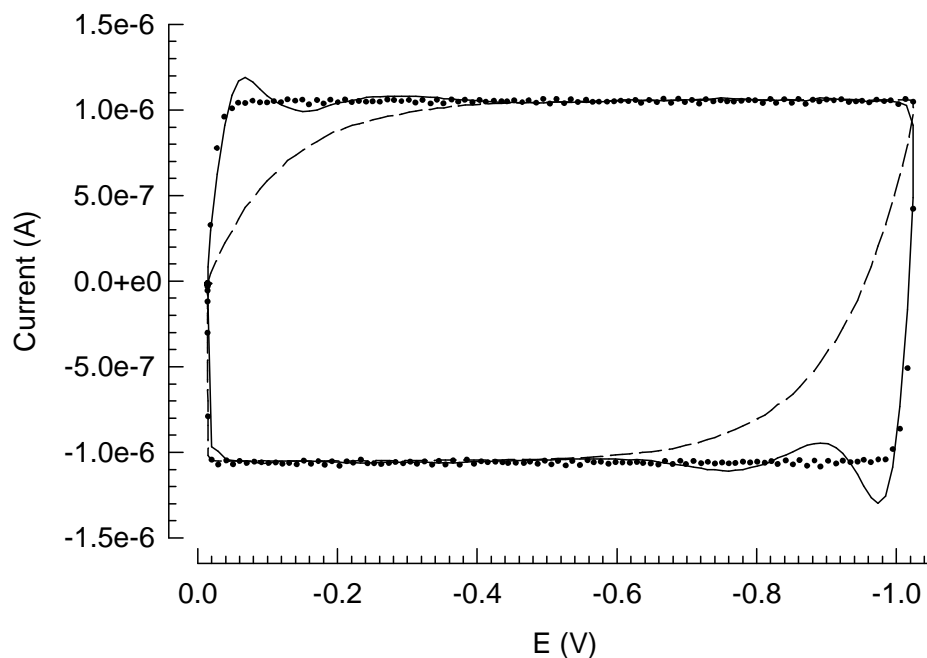
**Figure 2.** ICAP correction at dummy cell compared to a 0 Ω cell. (- - -) dummy cell from
Figure 1 response without correction (i.e. generation 0); (——) dummy cell from Figure 1 with
10 generations of ICAP correction; (···) response with 0 Ω resistance and 10.5 nF capacitance.

The ICAP method is shown in Figure 3a for an actual voltammetric experiment. It shows the oxidation
of 5.0 mM ferrocene in 0.5 M TBAPF$_6$/THF solution. The uncorrected voltammogram (generation 0) under
these conditions is essentially unusable. Scans up to generation 17 show the iteration process at work using
a compensation resistance, R$_{comp}$, value of 90 kΩ. The extent of the potential correction used during each
iteration step can be seen in Figure 3b. In this case over 1.0 V of correction is eventually required.

A concern with any form of ohmic-drop compensation is the possibility of over-correction. The ICAP
method can produce over-corrected voltammograms; however, it appears that any overcompensation will
be readily determined. An overcompensated voltammogram does not converge to a constant result with
continued iterations. It tends to diverge from preceding generations with an increasing amount of overshoot
and distorted peaks. These are simply the beginning of sustained oscillations that would occur if the
iterative process continued. Figure 4a, overcompensated at a R$_{comp}$ level of 22 kΩ, is a wave for the

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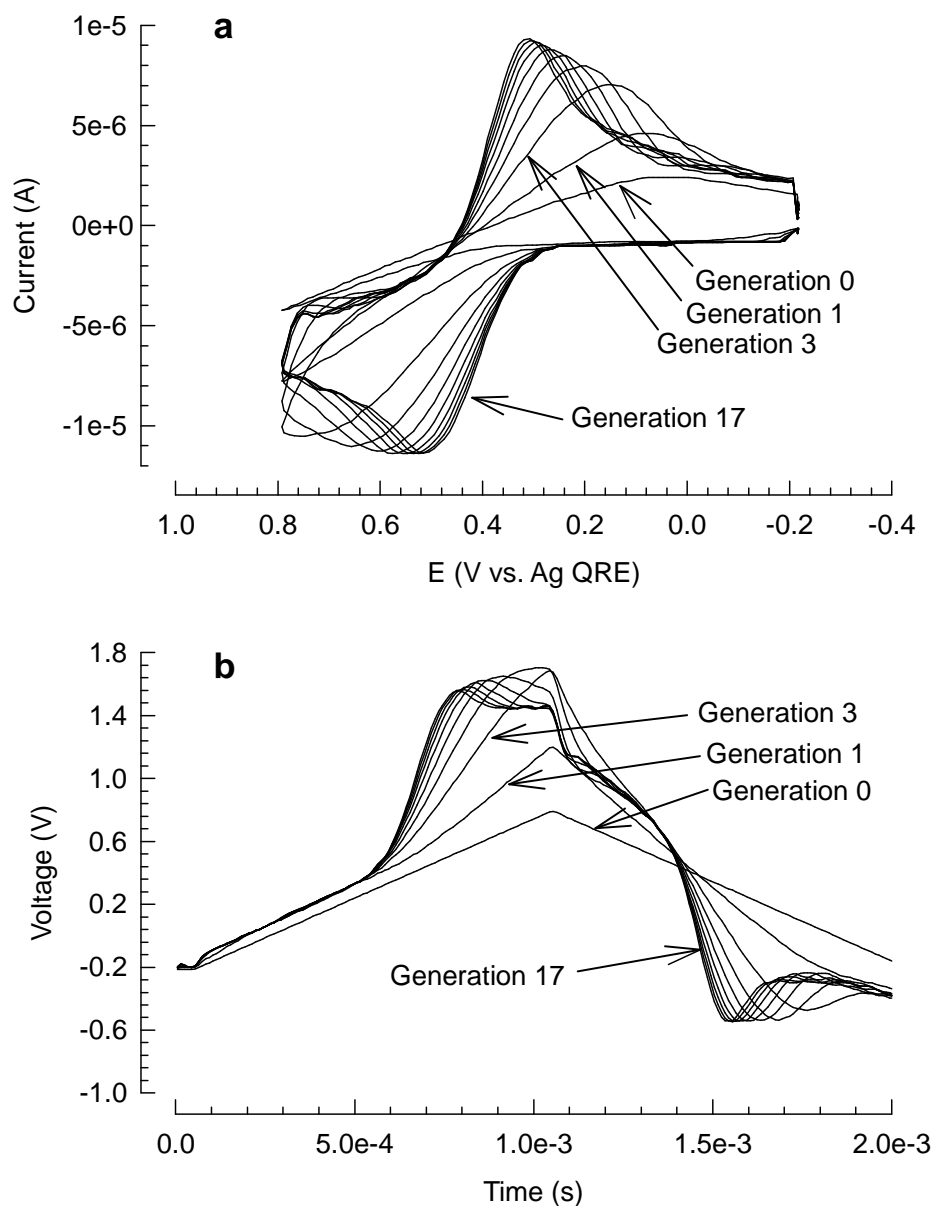**Figure 3.** ICAP correction applied to the cyclic voltammogram of 5 mM ferrocene in 0.1 M TBAPF$_6$ / THF solution. The scan rate is 1000 V/s. (a.) Current-potential curves for generations 0, 1, 3, 5, ... 17. The compensation level is 90 kΩ (90%). Note that the current is always plotted versus the generation 0 potential waveform. (b.) Applied voltage-time curves for the current-potential curves in (a.).
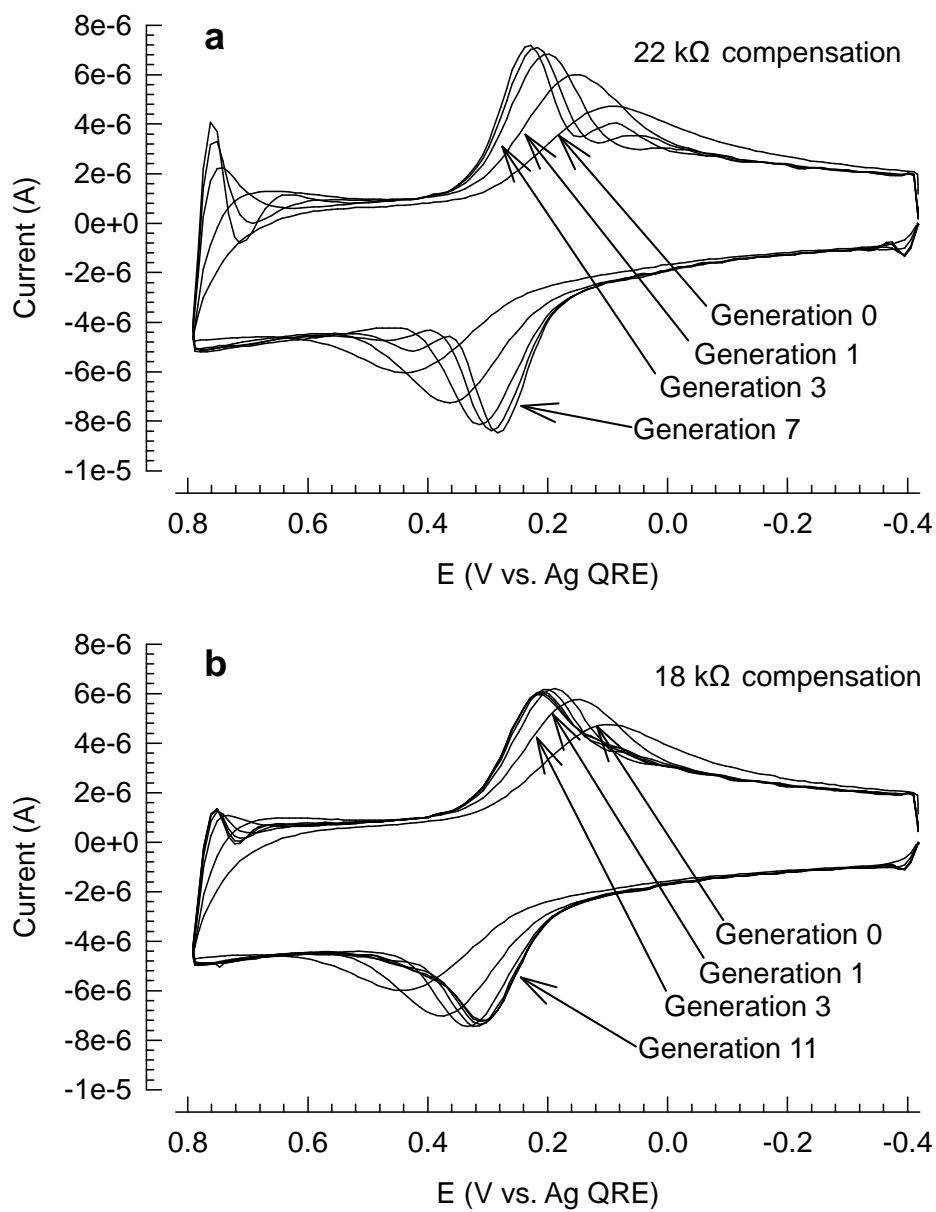
**Figure 4.** Voltammetry of 2 mM ferrocene in 0.5 M TBAPF$_6$ / THF solution at 1000 V/s showing the effect of correct compensation and overcompensation with the ICAP method. (a.) Voltammograms for generations 0, 1, 3, 5, 7 with compensation of 22 k$\Omega$ (110%). (b.) Voltammograms for generations 0, 1, 3, 5, ... 11 with compensation of 18 k$\Omega$ (90%).

oxidation of ferrocene in 0.5 M $TBAPF_6$ / THF. This wave shows a typical result of overcompensation: a large overshoot, oscillations following the forward and reverse peaks, and a "super-nernstian" peak separation of 55 mV. Note also that the overcompensation is apparent quite early in the iterative process. As little as five iterations is sufficient to determine that something is wrong with the wave. In contrast, Figure 4b is not overcompensated at a $R_{comp}$ level of 18 k$\Omega$ . Here, the overshoot does not tend to increase and the peaks are not distorted.

Although sustained oscillation can be produced with the ICAP method, it is unlikely to ever be a problem in actual use, since incipient oscillation is readily detected prior to its occurrence. This is in contrast to electronic positive-feedback compensation in which uncontrolled oscillation is an ever-present danger.

**Solution ac Impedance Measurements** ac impedance measurements were used to obtain an independent measurement of the cell resistance and double-layer capacitance. A graph of the cell impedance versus frequency and the best fit model values are shown in Figure 5. These data were acquired at the gold microdisk electrode in the three solutions used for the voltammetric measurements. The electrical model for the cell parameters is simple, a series combination of the solution resistance, $R_s$, and double-layer capacitance, $C_d$. In addition, it was found necessary to include in the model a small parallel shunt capacitance, $C_s$,  across the series $R_sC_d$ circuit. The effect of the shunt capacitance shows up as a decrease in impedance and phase shift at high frequencies. The shunt capacitance is apparently due to the capacitance of the electrode body. This effect is important in electrophysiological recording electrodes and has also been reported to be of concern for smaller diameter ultramicroelectrodes (dia. of less than 5 $\mu$m) (12). Although significant in the ac impedance measurements, the shunt capacitance has no effect on the relatively slow cyclic voltammetry reported here.

The double-layer capacitance was found directly from the low-frequency data (100 to 500 Hz). The capacitance value was then used as a non-adjustable parameter to find the resistance and shunt capacitance values from the impedance at higher frequencies. The estimated model parameters and their coefficients of variation (i.e. percent standard error) are summarized in Table 1. Note that the measured resistance will not depend on the working and counter electrode separation as long as that separation is more than 10 electrode radii(10), a condition easily met with the microelectrode used here.
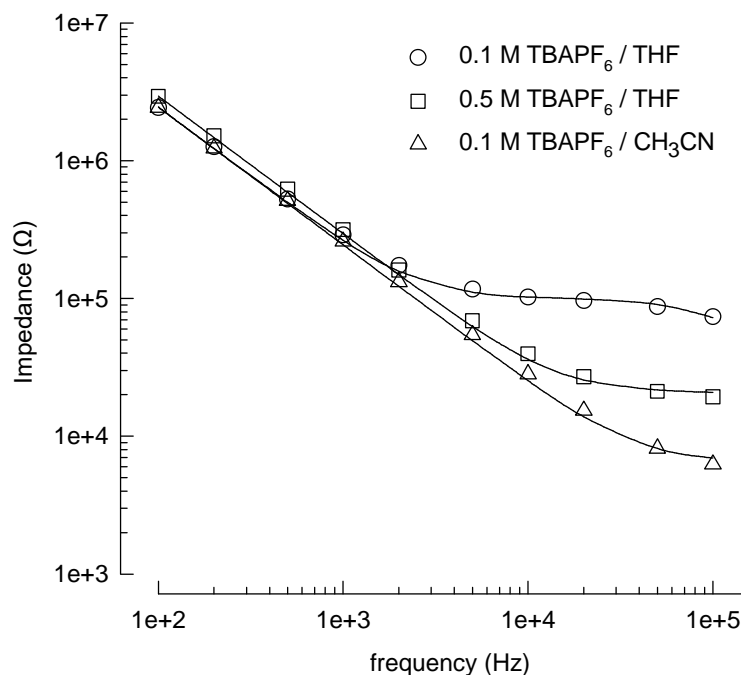
**Figure 5.** Impedance versus frequency for a 52-μm diameter gold disk electrode. (O, □, Δ): Experimental data for indicated solutions. (——) Model results from parameters given in Table 1.

**Table 1. Model Parameters for Solution Impedance Measurements**

| Solvent and Supporting Electrolyte | $R_s$ (kΩ) | $C_d$ (pF) | $C_s$ (pF) |
|---|---|---|---|
| THF with 0.1 M TBAPF$_6$ | $100 \pm 1.6\%$ | $650 \pm 18\%$ | 15 |
| THF with 0.5 M TBAPF$_6$ | $21 \pm 7\%$ | $540 \pm 18\%$ | 15 |
| Acetonitrile with 0.1 M TBAPF$_6$ | $6.5 \pm 13\%$ | $650 \pm 18\%$ | 15 |

**Simulation of ICAP Corrected Voltammograms**  The ability to correctly compensate for ohmic drop distortion was tested by simulation of the voltammetric waves both before and after ICAP compensation was applied. Figure 6a shows a simulation for the uncorrected response at 1000 V/s of 2 mM ferrocene in 0.1 M TBAPF$_6$ / THF. Simulation conditions are given in table 2. As can be observed, the fit between the experimental and simulated response is excellent for a $R_s$ value of 100 kΩ. Figure 6b shows the results with

ICAP compensation of 86 k$\Omega$ on the voltammetric wave. Here the simulation uses a $R_s$ value of 9.0 k$\Omega$ to get a very good fit to the experimental result. The main difference observed between the two results is the presence of a variable background current that is not simulated. The important result observed is the good agreement in the peak currents and peak separation. There is also a slight hump to the right of the reverse peak on the voltammetric wave. This is a residue of the iteration process and additional iterations would minimize these oscillations.

Simulation results for the three solvent systems at a range of scan rates are summarized in Table 2. For brevity, only the $\Delta E_p$ values are compared. All the simulations include the effect of quasi-reversible kinetics. Here, $k^0$ and $\alpha$ value were 3.0 cm s$^{-1}$ and 0.5, respectively. No specific experiments were performed to confirm that these are the most appropriate values, however, these values are similar to those reported for oxidation of ferrocene in $CH_3CN$ at a gold microelectrode[13] and, furthermore, good agreement between the experimental and simulated results are observed over a wide scan rate range.

Given these kinetic parameters it is clear that excellent agreement is observed for the uncorrected data in all three solvent systems. Particularly interesting is the good agreement between the $R_s$ values found by simulation and those found by ac impedance measurements (Table 2). Capacitance measurements with the two methods are quite different however. This is likely due to the fact that the ac measurements were made at the rest potential in a solution containing only supporting electrolyte.

Agreement between the corrected data and simulations are also very good, with one significant caveat. The amount of resistance required in the simulation to match the peak separation of the experimental data is less than is anticipated by a significant amount. For example, in the 0.1 M TBAPF$_6$ / THF data, the expected amount of resistance required would be the difference between the solution resistance (100 k$\Omega$) and the compensation amount (86 k$\Omega$), which would be 14 k$\Omega$. The best match for the simulation resistance is 9 k$\Omega$. Since the ac impedance and voltammetry both agree on the solution resistance and it is plain that the kinetic parameters are not at fault (even with reversible kinetics, the simulation peak separation is much larger than experimental for a 14 k$\Omega$ solution resistance), it is unclear why there is not better agreement. This is not a general problem, since the results for 0.5 M TBAPF$_6$ / THF agree nicely.
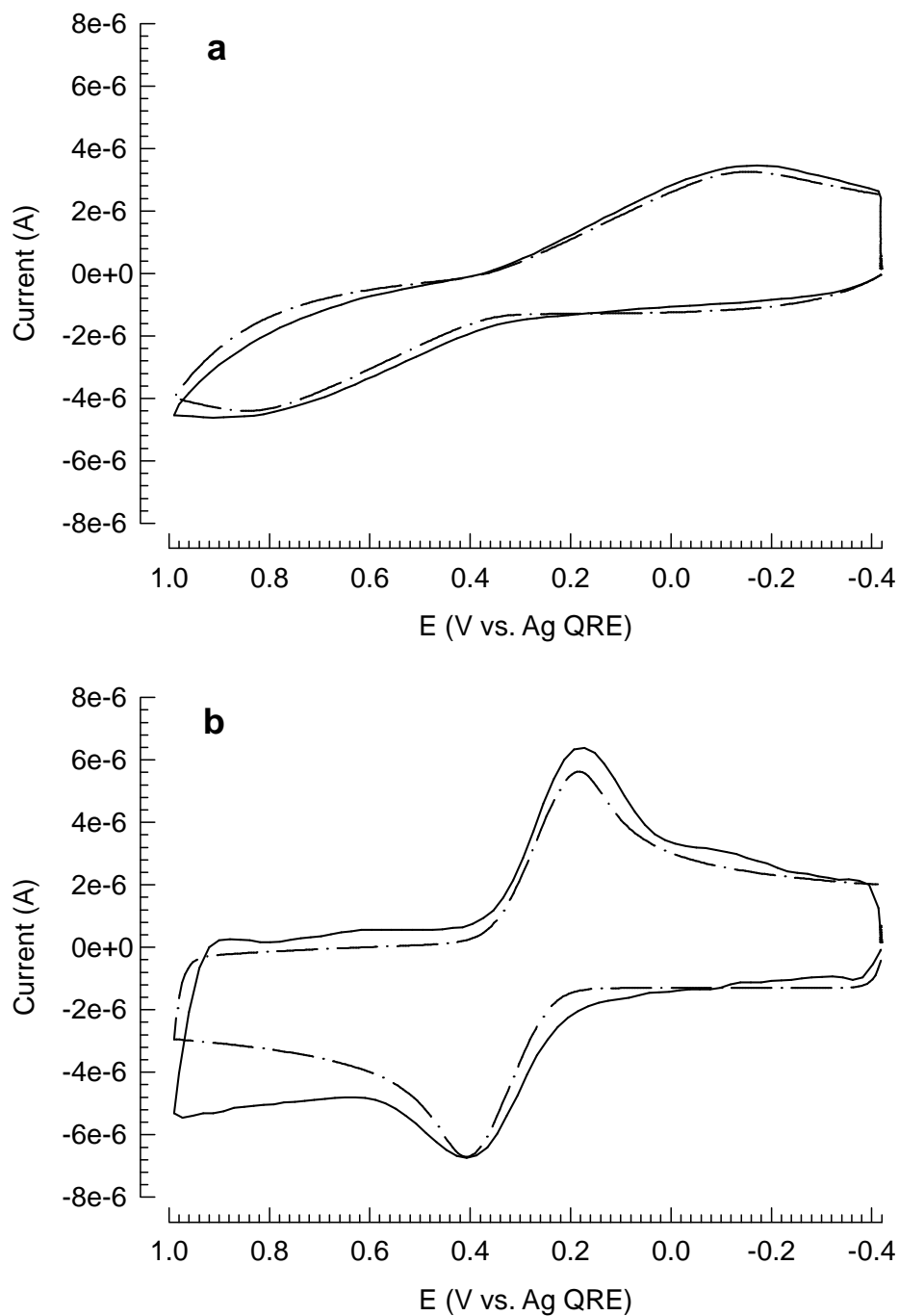
**Figure 6.** Experimental and simulated voltammetry of 2 mM ferrocene in 0.1 M TBAPF$_6$ / THF solution at 1000 V/s. (a.) (——) experimental data with no ICAP compensation. (– • –) simulation. Simulation parameters:  $D_o = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$; $C_o^* = 2 \times 10^{-6}$ mol cm$^{-3}$; $k^0 = 3$ cm s$^{-1}$; $\alpha = 0.5$; $E^0 = 0.290$ V; $C_d = 1.3$ nF; $R_s = 100$ k$\Omega$. (b). (——) experimental data with 86 k$\Omega$ of ICAP compensation. (– • –) simulation. Simulation parameters: as is (a) except $R_s = 9.0$ k$\Omega$.

**Table 2. Comparison of ICAP Uncorrected and Corrected data with Simulation**

| Solvent System | v (V/s) | Uncorrected | | | | Corrected | | | | |
| | | Data | Simulation | | | Data | | Simulation | | |
| | | $\Delta E_p$ (mV) | $\Delta E_p$ (mV) | $R_{s,sim}$ (kΩ) | $C_{d,sim}$ (nF) | $R_{comp}$ (kΩ) | $\Delta E_p$ (mV) | $\Delta E_p$ (mV) | $R_{s,sim}$ (kΩ) | $C_{d,sim}$ (nF) |
|---|---|---|---|---|---|---|---|---|---|---|
| THF 0.1 M[a] | 1000 | >1000 | 1001 | 100 | 1.3 | 86 | 234 | 226 | 9.0 | 1.3 |
| | 500 | 805 | 748 | 100 | 1.3 | 86 | 159 | 176 | 9.0 | 1.3 |
| | 100 | 421 | 418 | 100 | 1.3 | 86 | 117 | 110 | 9.0 | 1.3 |
| | 50 | 337 | 330 | 100 | 1.3 | 86 | 95 | 99 | 9.0 | 1.3 |
| THF 0.5 M[b] | 1000 | 347 | 316 | 20 | 1.0 | 17 | 95 | 99 | 1.6 | 1.0 |
| | 500 | 250 | 236 | 20 | 1.0 | 17 | 87 | 90 | 1.9 | 1.0 |
| | 200 | 180 | 175 | 19 | 1.0 | 17 | 80 | 80 | 1.9 | 1.0 |
| | 100 | 138 | 141 | 19 | 1.0 | 17 | 67 | 71 | 1.9 | 1.0 |
| CH₃CN 0.1 M[a] | 1000 | 227 | 204 | 6.6 | 2.0 | 5.2 | 74 | 82 | 0.5 | 2.0 |
| | 500 | 154 | 157 | 6.6 | 2.0 | 5.2 | 65 | 75 | 0.5 | 2.0 |
| | 200 | 116 | 116 | 6.6 | 2.0 | 5.2 | 63 | 69 | 0.7 | 2.0 |
| | 100 | 98 | 106 | 6.6 | 2.0 | 5.2 | 68 | 67 | 1.0 | 2.0 |

[a]Simulation parameters: $D_o = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$; $C_o^* = 2 \times 10^{-6}$ mol cm$^{-3}$; $k^0 = 3$ cm s$^{-1}$; $\alpha = 0.5$.
[b]Simulation parameters: as in [a] except $D_o = 1.4 \times 10^{-5}$ cm$^2$ s$^{-1}$.

## Conclusions

The ICAP method for correction of ohmic drop is a new and useful method. Although demonstrated here for correction of cyclic voltammetric data, there appears to be no barrier for implementation in chronoamperometric or cyclic staircase methods. There are at least two situations in which the ICAP method of ohmic drop correction would be preferred over conventional positive-feedback methods of correction. The first is at very short time scale measurements. Although positive feedback circuits for use with cyclic voltammetry at scan rates in excess of 100,000 V/s have been described(5, 6, 14), it is clear that it is technically challenging to design circuits that have sufficient bandwidth to support the positive feedback path without introducing additional distortion. In addition, the burden of designing the high-speed

circuit is left to the individual experimenter. It is doubtful that any commercial instruments will soon be available with this capability. In contrast, the ICAP method minimally requires a less complicated circuit (one op amp would suffice) to convert the current to a measurable voltage. The remainder of the setup requires only commercially available equipment. For the equipment used in this work, only the lack of a suitably wide bandwidth current transducer prevented operation to $10^6$ V/s.

The other situation in which the ICAP method would be useful is developing low-cost personal computer based instrumentation. In this case, the high-speed oscilloscope and arbitrary waveform generator is replaced with a single analog-to-digital / digital-to-analog board. It would be relatively straitforward to program the ICAP method for pc-based acquisition. Again, an advantage would be that the resulting analog instrumentation could be made simpler (i.e. cheaper). Alternately, existing potentiostats without built-in ohmic drop correction could be used directly with the ICAP method.

There are also situations where the ICAP process would be difficult or inconvenient to use. The most likely situation would be when the electrode response is not stable from scan to scan. For example, a deterioration of the response due to deposition of an insoluble product or a solution impurity on the electrode. In this case, repolishing the electrode after 1 or more iterations in the cycle may be necessary to achieve good results.

It should also be noted that the digital-based correction method lends itself to development of more efficient correction algorithms. For example, if $R_s$ and $C_d$ are known, the ICAP method can be modified to instantaneously correct for the ohmic drop caused by the charging current. Although not shown, this was done by calculating the capacitive current and adding it to the applied potential in the first generation. This method reduced the number of iterations required with the disadvantage of requiring specification of the experimental technique. It may also be possible to use the intermediate iteration results to make a prediction of the future wave shape. This predicted rather than the observed wave shape would be used to apply a correction voltage, with the net effect of a more efficient iteration process. It should be noted that only an approximation of the wave shape would be required since continued iterations would tend to improve subsequent wave shape predictions.

Finally, for measurements at short time scales, the response of the current transducer may cause additional distortion of the voltammetric wave (11). It has been previously shown that the distortion from a

limited current transducer bandwidth can be deconvolved from the data by use of fourier transform methods (11, 15). Since the ICAP method processes the data in a digital format, correction for this distortion can be directly incorporated into the ICAP method using the same methods. With a modern PC the fourier correction would add only a few 10's of milliseconds to the iteration cycle time.

## Acknowledgements

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