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ARTICLE *in* ANALYTICAL CHEMISTRY · JUNE 1996

Impact Factor: 5.64 · DOI: 10.1021/ac951209b · Source: PubMed

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Anal. Chem. 1996, *68*, 1871–1876

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

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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 are 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.

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 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 the work of others[1,2,6,7] that quite careful design and implementation of the positive feedback loop are 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 does 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 SECTION

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

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S0003-2700(95)01209-1 CCC: $12.00

pad and then 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 ($v \geq 50$ 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 Ω 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 V 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 ICAP method. A general outline of the steps required for the method is 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 waveforms 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 from the author.

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") are 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% compensations (after 10 generations) applied to the dummy cell and to a dummy cell with 0 Ω resistance is shown 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 iterations, but the minimum overshoot is still about 10%. Lower levels of compensation will further reduce the amount of overshoot.

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 overcorrection. The ICAP method can produce overcorrected voltammograms; however, it appears that any overcompensation will be readily determined. An overcompensated voltammogram does not converge to a constant result with

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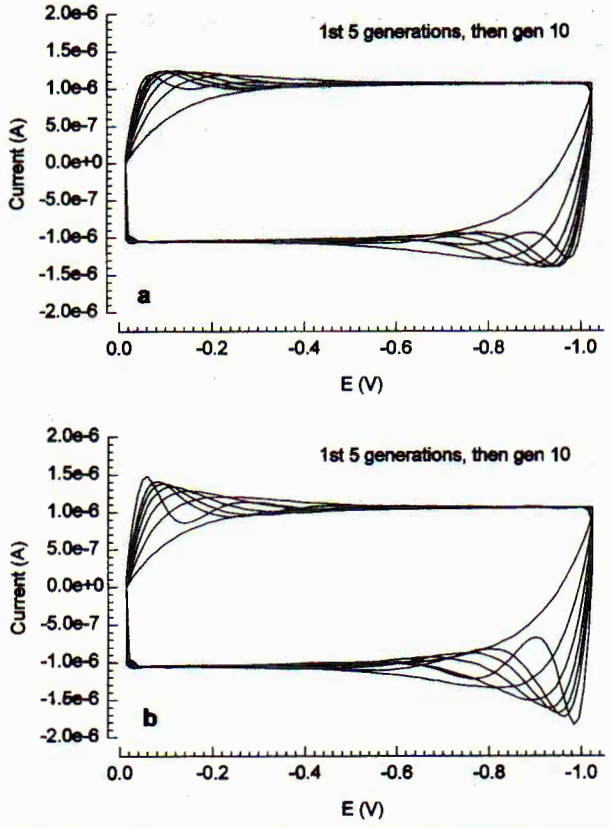

Figure 1. ICAP correction applied to cyclic voltage sweep applied to a dummy cell. Shown are the first five generations and then generation 10. Voltage sweep rate is 100 V/s. Dummy cell is a series resistor (100 kΩ) and capacitor (10.5 nF) in combination. (a) Compensation at 90 kΩ (90%) level. (b) Compensation at 100 kΩ (100%) level.

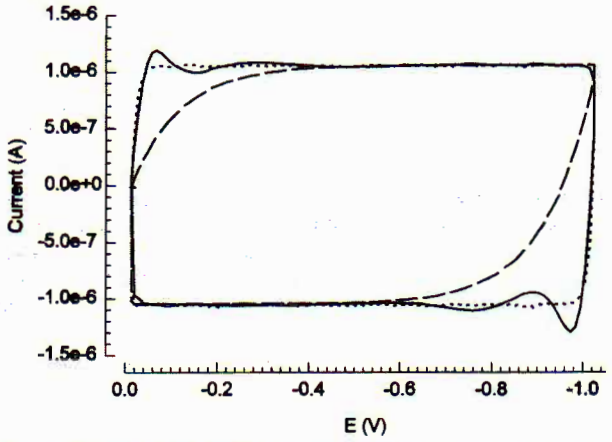

Figure 2. ICAP correction at dummy cell compared to a 0 Ω cell. (– –) Dummy cell from Figure 1 response without correction (i.e., generation 0); (–) dummy cell from Figure 1 with 10 generations of ICAP correction; (···) response with 0 Ω resistance and 10.5 nF capacitance.

continued iterations. It tends to diverge from preceding generations with an increasing amount of overshoot and distorted peaks. These are simply the beginnings 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 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

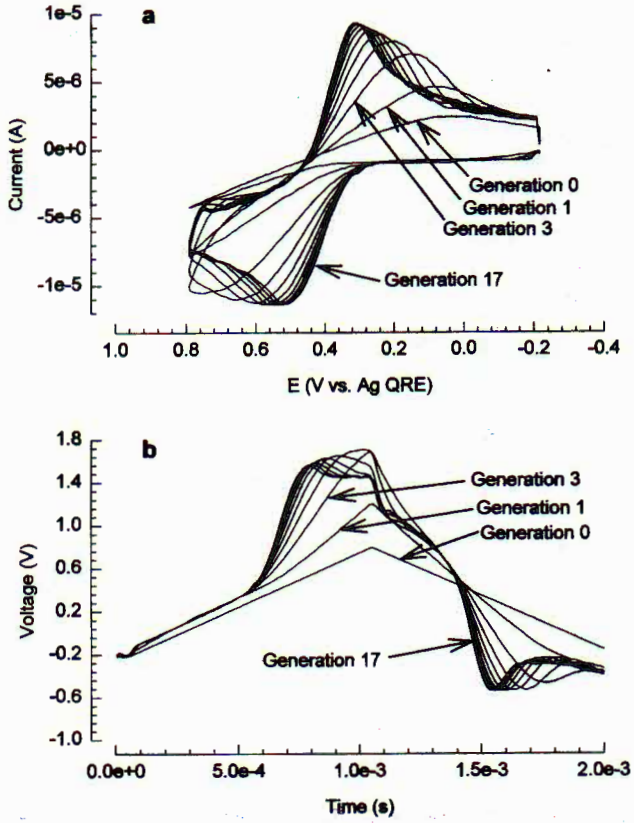

Figure 3. ICAP correction applied to the cyclic voltammogram of 5 mM ferrocene in 0.1 M $TBAPF_6$/THF solution. The scan rate is 1000 V/s. (a) Current–potential curves for generations 0, 1, 3, 5, ..., 17. The compensation level is 90 kΩ (90%). Note that the current is always plotted versus the generation 0 potential waveform. (b) Applied voltage–time curves for the current–potential curves in a.

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 kΩ. 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 an 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 to be 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 (diameter < 5 μm).[12] Although significant in the ac

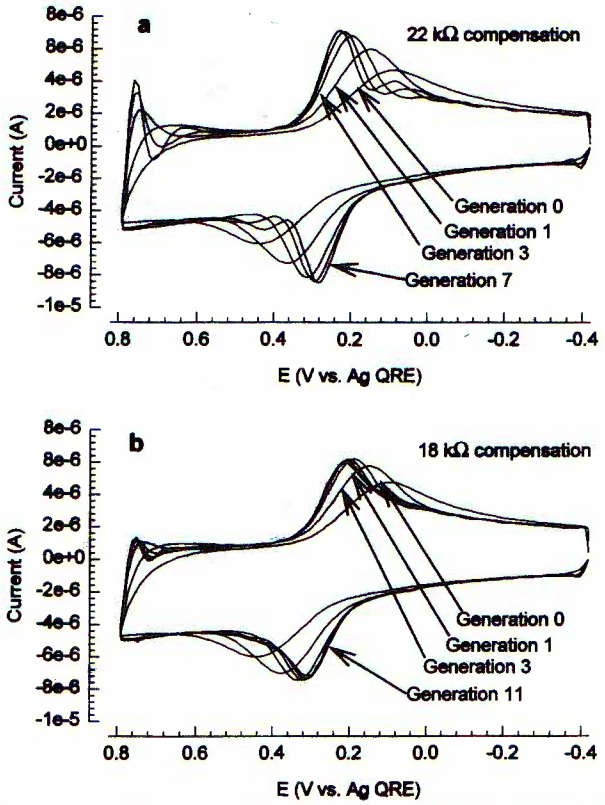

Figure 4. Voltammetry of 2 mM ferrocene in 0.5 M $TBAPF_6$/THF solution at 1000 V/s showing the effect of correct compensation and overcompensation with the ICAP method. (a) Voltammograms for generations 0, 1, 3, 5, and 7 with compensation of 22 kΩ (110%). (b) Voltammograms for generations 0, 1, 3, 5, ..., 11 with compensation of 18 kΩ (90%).

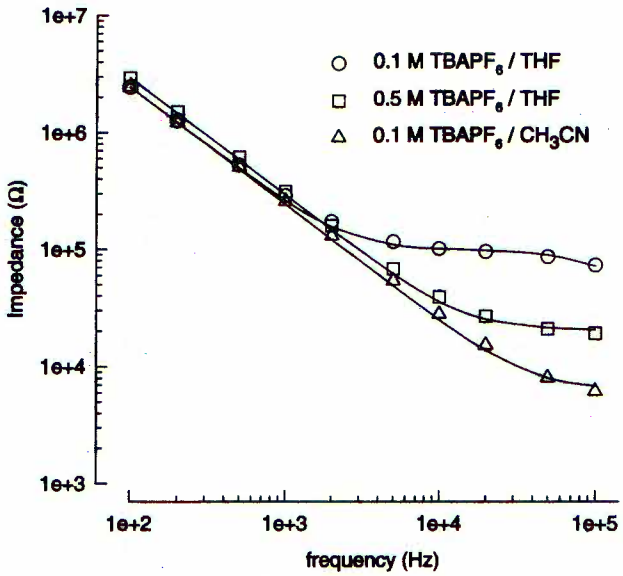

Figure 5. Impedance versus frequency for a 52 μm diameter gold disk electrode. (○, □, △): Experimental data for indicated solutions. (—) Model results from parameters given in Table 1.

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 (100–500 Hz). The capacitance value was then used as a nonadjustable 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.

Table 1. Model Parameters for Solution Impedance Measurements

solvent and supporting electrolyte	R_s (kΩ)[a]	C_d (pF)[a]	C_s (pF)
THF with 0.1 M $TBAPF_6$	100 ± 1.6	650 ± 18	15
THF with 0.5 M $TBAPF_6$	21 ± 7	540 ± 18	15
acetonitrile with 0.1 M $TBAPF_6$	6.5 ± 13	650 ± 18	15

[a] Values are given ± percent standard error.

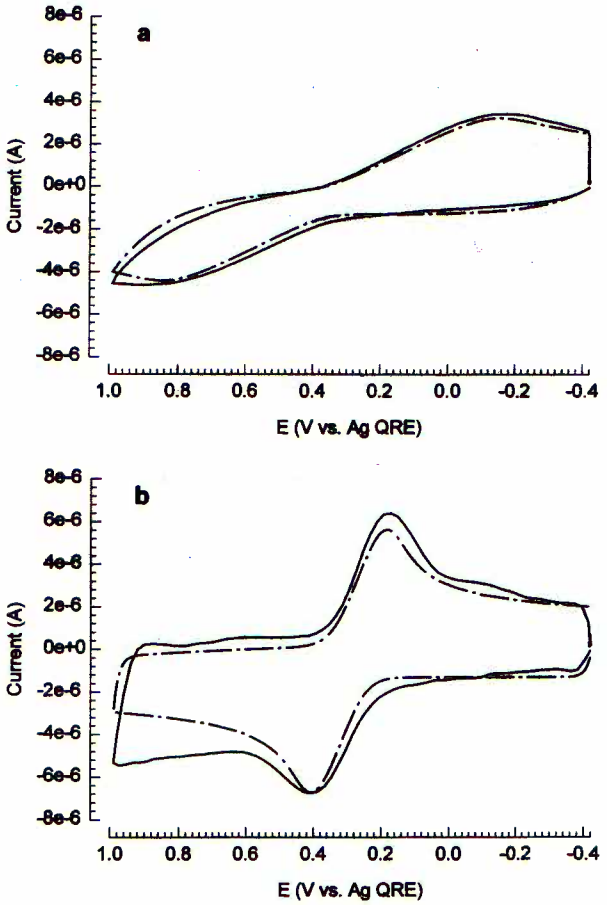

Figure 6. Experimental and simulated voltammetry of 2 mM ferrocene in 0.1 M $TBAPF_6$/THF solution at 1000 V/s. (a) (—) Experimental data with no ICAP compensation. (—·—) simulation. Simulation parameters: $D_o = 2 \times 10^{-5}$ cm^2 s^{-1}; $C_o^* = 2 \times 10^{-6}$ mol cm^{-3}; $k^o = 3$ cm s^{-1}; $\alpha = 0.5$; $E^o = 0.290$ V; $C_d = 1.3$ nF; $R_s = 100$ kΩ. (b) (—) Experimental data with 86 kΩ of ICAP compensation. (—·—) simulation. Simulation parameters are as is a, except R_s = 9.0 kΩ.

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.

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Table 2. Comparison of ICAP Uncorrected and Corrected Data with Simulation

		uncorrected				corrected				
		data	simulation			data		simulation		
solvent system	v (V/s)	ΔE_p (mV)	ΔE_p (mV)	$R_{s,sim}$ (kΩ)	$C_{d,sim}$ (nF)	R_{comp} (kΩ)	ΔE_p (mV)	ΔE_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
CH_3CN 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}; $k^\circ = 3$ cm s^{-1}; $\alpha = 0.5$. [b] Simulation parameters as in a except $D_o = 1.4 \times 10^{-5}$ cm^2 s^{-1}.

Figure 6b shows the results with ICAP compensation of 86 kΩ on the voltammetric wave. Here the simulation uses a R_s value of 9.0 kΩ 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 ΔE_p values are compared. All the simulations include the effect of quasi-reversible kinetics. Here, k^0 and α values 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 is 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 is 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 kΩ) and the compensation amount (86 kΩ), which would be 14 kΩ. The best match for the simulation resistance is 9 kΩ. 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 kΩ 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.

CONCLUSIONS

The ICAP method for correction of ohmic drop is a new and useful method. Although it is 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 in developing low-cost personal computer based instrumentation. In this case, the high-speed oscilloscope and arbitrary waveform generator are 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.

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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, e.g., 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 one 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, then 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 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 tens of milliseconds to the iteration cycle time.

ACKNOWLEDGMENT

D.O.W. gratefully acknowledges the donors of The Petroleum Research Fund, administered by the ACS; the state of Mississippi; and the NSF EPSCoR Program (Grants EHR-9108767 and OSR-9452857) for support of this research.

Received for review December 14, 1995. Accepted March 25, 1996.[•]

AC951209B

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