

Application Note



Subject: Fast Scanning Electrochemistry with the 283/PARSTAT 2273

INTRODUCTION

One of the selling features of the 283 and PARSTAT 2273 potentiostats is their excellent high frequency response. Many customers have taken advantage of this frequency response using either the PARSTAT 2273 with its built in Frequency Response Analyzer or the 283 in conjunction with a 1025 Frequency Response Analyzer and PowerSINE™ Impedance software. However, customers who wish to use a microelectrode and perform fast cyclic voltammetry will also see the benefits of this frequency response. The upper useable limit of these systems is between 50,000 and 100,000 V/sec. With these high scan rates, one may study reactions and electrochemically generated intermediates with half-lives as short as 10 μ sec!

BACKGROUND

In the world of electrochemistry with microelectrodes, there are two different types of response: steady state microelectrode voltammetry and fast scan cyclic voltammetry. For steady state microelectrode voltammetry, the current response is an S-shaped, sigmoidal curve, reminiscent of classical DC polarography. The height of the diffusion-limited plateau is independent of the scan rate and is proportional to the radius of the microelectrode. Since current may be nanoamperes or less for a 10 μ m diameter electrode, the 283 with its 1 nA current range or the 2273 with its 2 nA current range are excellent choices for these experiments. This steady state behavior is observed for scan rates of about 10 mV/sec or less (see Figure 1).

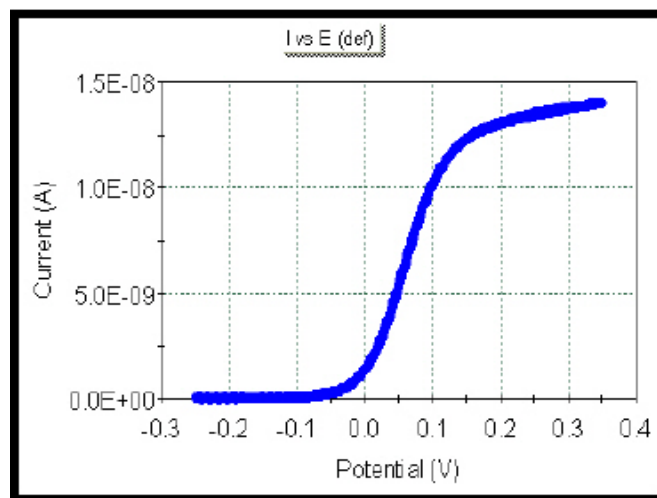


FIGURE 1: Ferrocene (5 mM) at 10 mv/sec. Data was taken with a 283 and PowerCV™ software using a 10 μ m diameter Pt microelectrode.

However, at scan rates above 1 V/sec the cyclic voltammograms begin to show the “peak” behavior that we generally associate with cyclic voltammetry at large electrodes (see Figure 2). At high sweep rates, the peak current is proportional to the square root of the sweep rate ($v^{1/2}$), just as it is for a classical cyclic voltammogram with a conventionally sized electrode. Researchers who wish to study very fast chemical or electrochemical reactions will use a microelectrode in its “fast scan” mode. The duration of their experiments must be about equal to the half-time of the reactions they wish to study. For a reaction with a half-time of 10 μ sec, scan rates as high as 100,000 V/sec must be used. Reactions of this speed may be found in many application areas. A leading company in instant photography was interested in fast scan voltammetry so that they could study the fast reactions (and harmful side reactions) of the photosensitive dyes in the film following its exposure to

light. They were so interested that they sent a chemist to an ACS electronics short course so she could build a fast potentiostat! Fast scan cyclic voltammetry has also been used to study the first stages of the formation of electroactive or conducting polymers¹ and in studying the electron transfer in conducting polymers.² The reactions of unstable cation radicals also have been studied using fast scan voltammetry.³ Examples can also be found in the area of photovoltaic cells for use in solar power applications.⁴

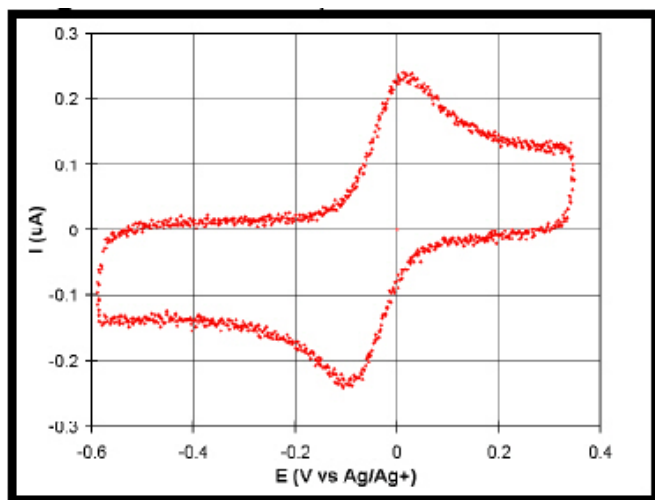


FIGURE 2: Same conditions as Figure 1 with a scan rate of 2000 V/sec.

EVALUATING THE 283 FAST SCAN CAPABILITES

A series of tests were performed to evaluate the capability of the 283 to perform fast scan cyclic voltammetry and to measure its performance. While the experiment described below was performed using a 283, the PARSTAT 2273 could easily be substituted in the same setup to perform the measurements. These test were performed using a 283 (S/N 24103), a Tektronix TDS 3054 digital storage oscilloscope and a Krone-Hite KH 5400B analog waveform generator. A typical setup is diagrammed in Figure 3. The tests were all performed using the 283 in the “four electrode mode” to eliminate the effects of stray cable capacitance. The working electrode lead (coax) and working sense input (from the buffer “pod”) were connected directly and independently to the cell in use. The counter electrode lead (coax) and reference electrode input (from its “pod”) were connected in normal fashion.

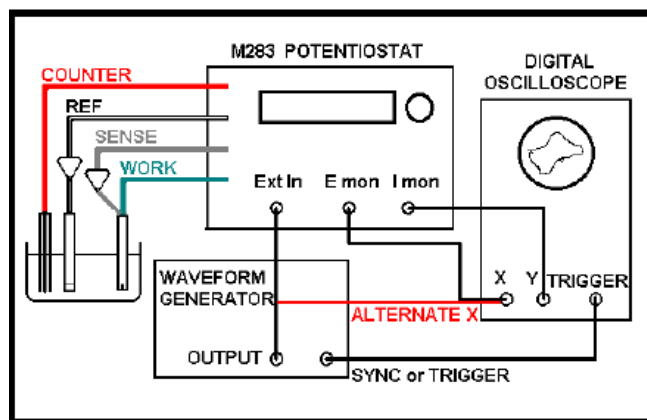


FIGURE 3: Connecting the M283, Generator and Oscilloscope. The scope’s X channel can alternatively be driven by the generator output.

The first test was designed to show the voltage response of the 283 under fast scan conditions. A 10 Ω resistor was chosen as the cell and the tests were run on the 100 mA scale. The waveform generator was set up to generate a 500 mV peak-to-peak triangle wave at 100 kHz. This corresponds to a scan rate of 100,000 V/sec (a 500 mV scan up and a 500 mV scan down in 10 μ sec). The result of this test is shown in Figure 4. The red line shows the output of the waveform generator connected directly to the oscilloscope, while the blue line shows the 283 response measured at the E Monitor BNC on the front panel. Except for some rounding at the apex of the triangle wave, the 283 follows this 100,000 V/sec scan rate quite nicely. This test evaluates the external input circuitry, the power amplifier, the electrometer and the E Monitor circuitry of the 283, used as a system.

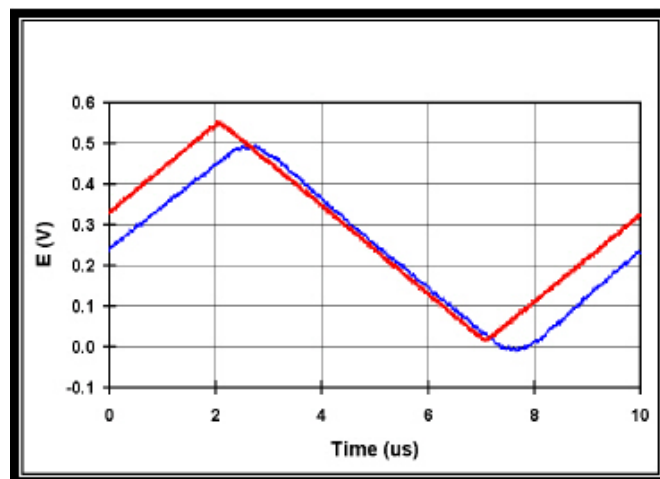


FIGURE 4: Generator output (red) and 283 E Monitor (blue) signals.

A second electrical test cell was chosen to more closely approximate the “real life” use of a 283 in a fast scan application. While the charging current for a microelectrode is quite small when it is used in the steady state regime (slower than 10 mV/sec), it becomes very significant at the scan rates in fast scan cyclic voltammetry (faster than 1000 V/sec). Consequently, for our test of speed, a small capacitor was selected as an electrical model for the cell. A value of 68 pF was selected, somewhat arbitrarily, but in the range of 20-80 pF that might be observed for a 10 μm diameter microelectrode.

Figure 5 shows a scan run at 100,000 V/sec on this capacitor using the 283 on the 100 μA scale. For the triangular waveform, the theoretical charging current curve should look like a rectangle. The current should have a constant value equal to the positive charging current during the anodic portion of the scan and the constant negative charging current when the potential is swept in the opposite direction. The observed “ringing” at the extremes of the scan in Figure 5 is typical of a fast potentiostat’s response to a nearly step change in current, from -7 to +7 μA . The ringing dies away quickly, however, and the charging current is fairly constant over the major portion of the scan.

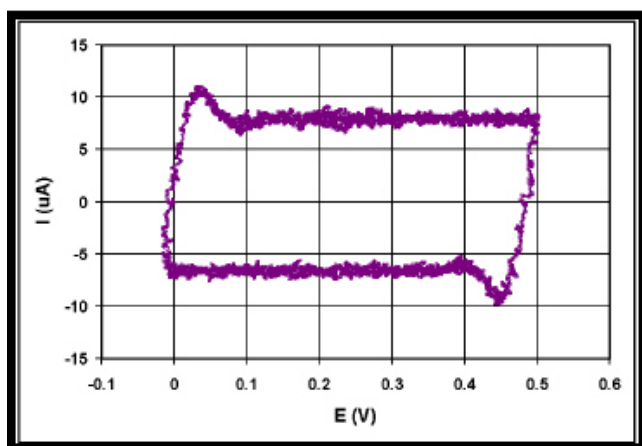


FIGURE 5: M283 at 100,000 V/sec. The cell is a 68 pF capacitor.

The size of the current deserves some mention. For a capacitor, the charging current can be calculated from the scan rate (dE/dt) and the capacitance:

$$I = C (dE/dt)$$

For $C = 68 \times 10^{-12}$ F and $dE/dt = 10^5$ V/sec, the calculated current is 6.8×10^{-6} A, in good agreement with the 7-8 μA that can be read from the charging current plateaus in Figure 5.

A TEST WITH A REAL ELECTROCHEMICAL CELL

Testing an instrument with an electrical circuit is convenient but it is not as convincing as using a real electrochemical cell! Several scans were run using a 10 μm diameter platinum microelectrode (G0225). Ferrocene (5 mM) dissolved in acetonitrile was used. The supporting electrolyte was 0.1 M tetraethyl ammonium perchlorate (TEAP). A non-aqueous reference electrode (Ag/0.1 M Ag^+ , K0103 with G0155 Non-Aqueous Filling Solution) was used.

A scan run under these conditions at an intermediate scan rate (2,000 V/sec or 2kV/sec) is shown in Figure 2. The separation between the anodic and cathodic peaks is about 100 mV, in tolerable agreement with the theoretical value of approximately 60 mV. Obtaining theoretical values of peak separation can be quite demanding. Adsorption of trace impurities and “fouling” of the electrode can easily distort the theoretical shape of the CV. The data shown here was for a freshly polished electrode. Curve shapes degraded upon standing and continued cycling and the electrode had to be repolished every few minutes.

At 2 kV/sec, the difference between the anodic and cathodic currents at a single potential can be used to estimate the electrode’s capacitance using the equation above. From the measured difference of 0.0148 μA at -0.450 V, the electrode’s capacitance is calculated to be 37 pF. This is in good agreement with the value of 15 pF calculated by assuming a capacitance of 20 $\mu\text{F}/\text{cm}^2$ for a 5 μm radius electrode. Unless extra precautions and shielding are employed, stray capacitance of the microelectrode’s wires and the glass construction can easily add 10 pF to the experimental measured capacitance!

At 20 kV/sec, the results are similar but it becomes a little more difficult to distinguish between the faradaic and charging currents (see Figure 6). The charging current (as measured by the separation between anodic and cathodic half cycles at -0.4 V) has increased by a factor of nearly 10 (to 1.24 μA , equivalent to a capacitance of 31 pF). The anodic faradaic peak current has increased only

by a factor of about 3 ($=10^{1/2}$!) from 0.22 to 0.59 μA . This, of course, is the classical problem of charging current. Charging current increases in direct proportion to the scan rate, v , while the faradaic current (peak current) only increases as $v^{1/2}$. Eventually, the charging current will obscure the faradaic current of interest!

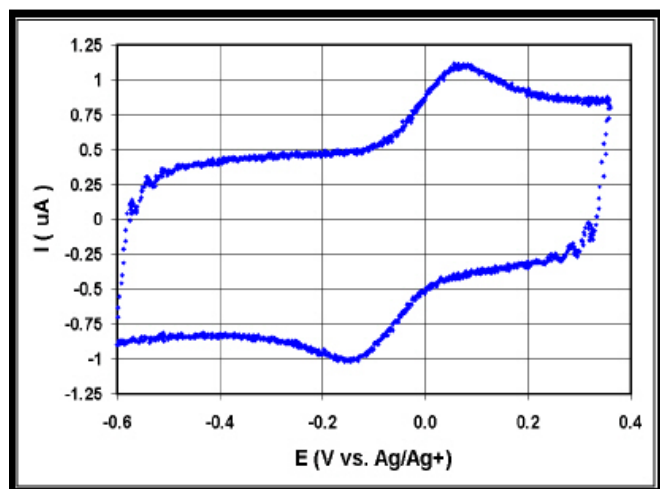


FIGURE 6: Ferrocene at 20 kV/sec. Recorded on the 10 μA scale.

Doubling the scan rate to 40 kV/sec (see Figure 7) nearly reaches this limit! Although there is clear evidence for the presence of an electroactive species, a peak is no longer clearly defined. Moreover, the ringing present at the sweep reversal points seems to extend over a larger voltage range than in Figure 6 (20 kV/sec).

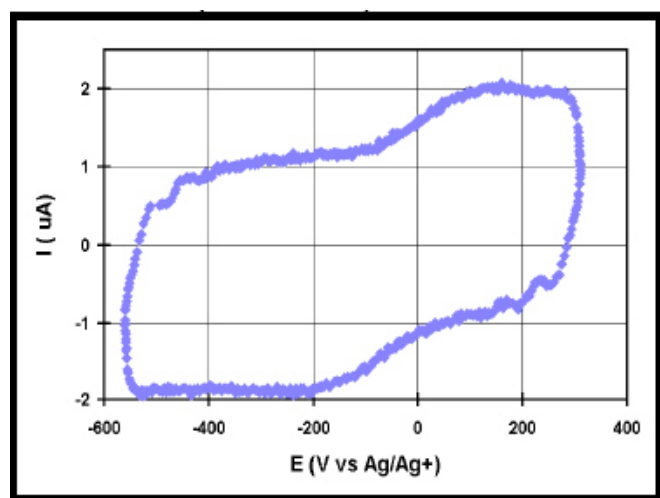


FIGURE 7: 40 kV/sec on the 100 μA scale. An I/E filter setting of 15 pF was used.

The ringing lasts for about the same length of time in Figures 6 and 7. However, because the scan rate is twice as big in Figure 7 as in Figure 6, the ringing stretches over twice the voltage and it is more noticeable in a typical CV scan. Finally, at 60 kV/sec (Figure 8) the ringing dominates the CV and, for this cell, it defines the upper limit of the scan rate. Other cells or electrodes may exhibit this behavior at a somewhat different scan rate.

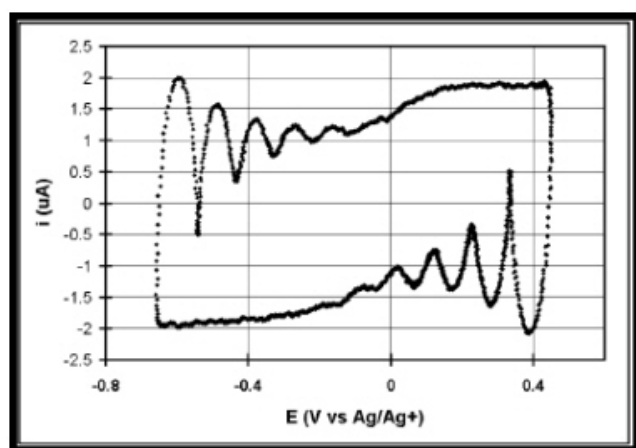


FIGURE 8: 60 kV/sec on the 100 μA scale. No I/E filter was used.

SELECTION OF CURRENT RANGE

The selection of the current scales used in these experiments may seem inappropriate or less than optimal. It is true that the currents in these scans are only a few percent of the full-scale current. However, when selecting a current range for these fast scan rate voltammograms, one must consider not only the magnitude of the current but also the frequency response (speed) of each current scale. Due to stray capacitances and stability design considerations, the most sensitive current ranges are also the slowest responding. The sharp change in the current at the voltage reversal points of the voltammogram can be used as a fairly realistic gauge of the distortions due to slow I/E response. The voltage extrema should not be overly rounded or distorted.

Additionally, the effects of the I/E filter setting become more severe as the current range is made more sensitive. The amount of filtering increases with increasing values of the $R_m C$ product. R_m is the value of the current measuring resistor in the potentiostat (e.g., 1 M Ω for the 1 μA scale) and C is the value of the capacitor selected by the I/E filter setting. For the 283, available values are 15

pF, 470 pF and 15 nF. If the product of scan rate (v), R_m and C is more than a few mV, use of the filter may distort the voltammogram. For reference, this product is 9 mV at 60 kV/sec on the 100 μ A scale ($R_m = 10$ k Ω) using the smallest capacitor, 15 pF. Using any I/E filter at this scan rate and current range is marginal!

CAVEATS AND PITFALLS

Besides these questions of selecting the current range and filtering, there are a few additional considerations when performing fast scan cyclic voltammetry. Unlike slow scan voltammetry on microelectrodes, the uncompensated resistance can play an important role at the fastest scan rates. The small size of the microelectrode leads to a moderate uncompensated resistance that increases linearly as the electrode radius shrinks. The peak separation has increased to about 300 mV in Figure 7 from 100 mV in Figure 2. Although quasi-irreversibility may be responsible for some of this change, uncompensated resistances in the range of 10-50 k Ω are reasonable guesses. If positive feedback iR compensation is used, the alternative connection for the oscilloscope's X (voltage) channel (as shown in Figure 3) is preferred.

Some care must also be paid to the selection of the oscilloscope's sampling rate or timebase. Looking only at the I vs. E traces on the oscilloscope can be misleading and it is easy to be fooled (as we were)! To capture a single cycle with millivolt resolution at 50 kV/sec requires sampling a point every 20 nsec. Luckily, newer digital oscilloscopes are up to this task, older ones may not be.

The subtraction of the background current, which is almost entirely the charging current, is advantageous and required for kinetic studies. However, fouling of the electrode makes it difficult to do successfully in a "batch" mode. Using a microelectrode in a traditional electrochemical cell, such as the K0235 Microcell, does not work well. Moving the electrode from pure supporting electrolyte (to record the charging current background) to a solution containing the electroactive species may expose the electrode to the air, trace impurities or adsorbents that might change the background. Although one might perform all the experiments in an inert atmosphere in a dry box, a simpler solution has been used.⁶ The microelectrode is placed in a flow injection (FIA) system. A background scan is recorded while pure supporting electrolyte is flowing past the electrode. A bolus of a similar solution, containing the electroactive species of interest, is injected and a voltammogram is recorded as the bolus passes by the

microelectrode. Due to the high diffusion rate at a microelectrode, the voltammograms are unaffected by a modest flow rate of the electrolyte.

The solutions used in these tests contained 5 mM Ferrocene. A higher concentration might allow reasonable scans at a higher scan rate, but higher concentrations may not be feasible or desirable in the electrochemical system of interest. Lower concentrations will lead to lower maximum scan rates. The concentration selected here was chosen as a happy medium.

SUMMARY

The 283 performs well for microelectrode studies in both the slow scan, steady state regime and the fast scan mode. The fast scan results shown here agree well with the theoretical limits based on charging current and iR drop contributions.⁷ Fast cyclic voltammetric studies with the PARSTAT 2273 or 283 are a good tool for studying electronically excited, highly reactive species that are important in the areas of photochemistry, solar energy production, biochemistry, free radicals, photosynthesis and electroactive and conducting polymers.

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