Introduction

The primary purpose of a potentiostat is to control the potential (voltage) of an electrochemical cell while measuring the current response. Current flowing through a resistor is directly proportional to the voltage difference across that resistor, as defined by Ohm's law ($E = IR$). A potentiostat forces the current to flow across a resistor (R_m) and measures current by the resulting voltage drop across R_m.

The current range defines the maximum amount of current that can be measured and the accuracy of a given potentiostat as a function of its available ranges. Princeton Applied Research offers an array of choices, all of which include the option to auto range, while the specific ranges depend on the instrument model. By selecting the current range according to best practices, the user is able to take full advantage of the potentiostat's capabilities.

Auto ranging allows the instrument to dynamically adjust the ideal range throughout the experiment. So that, at any given time, the instrument selects the lowest range for which the measured current will not exceed the range magnitude.   The advantage of auto ranging is high accuracy and resolution throughout the experiment and reduced noise. One disadvantage is the possibility of data spikes, which typically arise when performing fast potential pulse/step or voltammetry experiments or when using a highly capacitive electrode. The origin of the spikes is best explained by considering how the current is measured within most Princeton Applied Research potentiostat/galvanostat systems.

An electronic circuit called a current-to-voltage converter, or simply I/E converter (Fig. 1), is responsible for measuring current. The partial block diagram in Fig. 1 shows several highly accurate resistors as part of the I/E converter, each of which represents an available current

range (in this example, 20 nA to 2 mA). Any of the available current ranges can be selected for continuous use throughout an experiment. This is referred to as a fixed current range, as opposed to auto range. In either case, the current passes across one of these resistors such that a voltage of reasonable magnitude can be measured across that resistor. Thus, currents are measured via voltage measurements across Rm. Recalling Ohm's Law, a low current (100 μA) across a large value R_m (10 kΩ) produces a larger voltage (1 V) compared to passing that same current across a small value R_m (10 Ω, $E = 1$ mV). This explains why the value of R_m increases as the current range decreases.

The "Auto" range setting uses a series of relays to switch from one R_m to another. As one current range begins to lose accuracy due to low current (thus, low voltage) across a given R_m, a relay switches to a greater magnitude R_m, thereby increasing the voltage and providing greater accuracy in measuring the lower current. For example, a
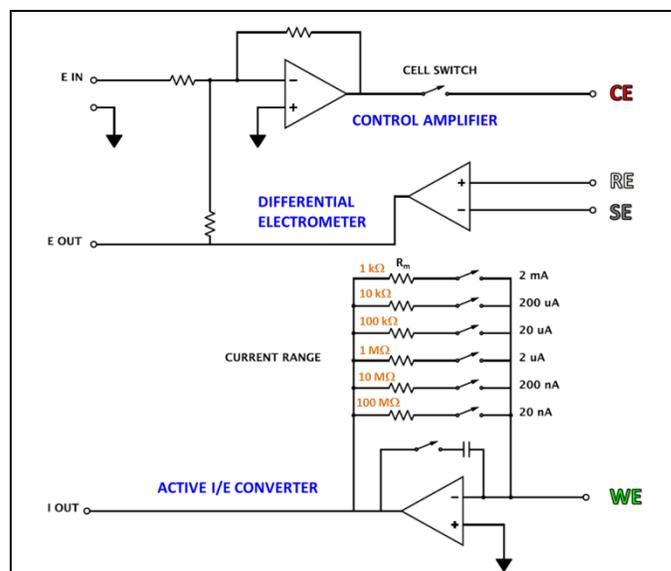
Figure 1: Typical potentiostat block diagram

10 μA current flowing across the 2 mA range (R = 1 kΩ would produce a voltage of 10 mV; switching that same current across the 200 μA range (R = 10 kΩ) increases the voltage to 100 mV, which can be measured with greater accuracy and precision. When the current increases and a current overload is detected, the circuit behaves accordingly, switching to an appropriate higher range with a smaller magnitude R_m.

Practical Examples

With a basic understanding of the potentiostat's hardware that is responsible for measuring current, we can use Cyclic Voltammetry (CV) to demonstrate how the Current Range setting can affect the resulting data. VersaStudio allows the user to select between two voltammetry Actions: Staircase Voltammetry and Cyclic Voltammetry. The data included in this document were collected using the latter Action, which is designed to mimic an analog ramp generator by automatically making the potential step size as small as possible, using a maximum of 1000 points per scan or 2000 per CV. Note that Staircase Voltammetry allows the user to control the number of points collected by defining a step height and time. All CVs were collected using a micro-cell kit (K0264), Au milli electrode (G0227) and Pt wire counter electrode (K0266). All potentials reference a Ag/AgCl reference electrode. The solution was 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl.

Fig. 2 shows 3 CVs run on the same cell at 100 mV/s, using various settings. Fig. 2 (A) was collected using the I Filter set to 10 Hz and Current Range set to "Auto", while Fig. 2 (B) used the same I Filter and a 20 μA fixed current range. The I Filter and Current Range were both set to "Auto" in Fig. 2 (C), where the "Auto" I Filter setting is 1 kHz. Fig. 3 shows the *Experiment Properties* window with the *Advanced Properties* view enabled, where these settings were assigned.

Let's first consider why there are spikes in the data shown in Fig. 2 (A). If the raw data are examined more closely, it is clear that the spikes occur when the current range (*I Range*) switches from one range to the next.

Fig. 4 shows the current spike at ~ 270 mV observed in the negative going scan from Fig. 2 (A) and the corresponding raw data. Prior to the spike, the current is measured on the 2 μA range as −1.833 μA. When the current increased beyond 2 μA, the relay switched to the 20 μA range, resulting in a spike to −15.865 μA. **The**

(A) I Filter = 10 Hz, Current Range = "Auto"
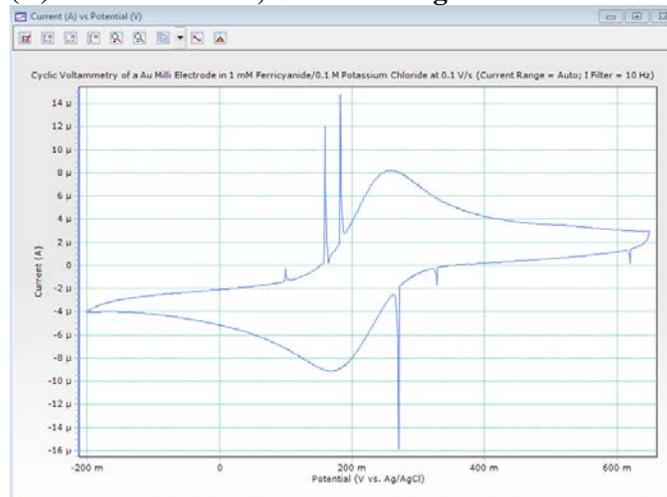
(B) I Filter = 10 Hz, Current Range = 20 μA
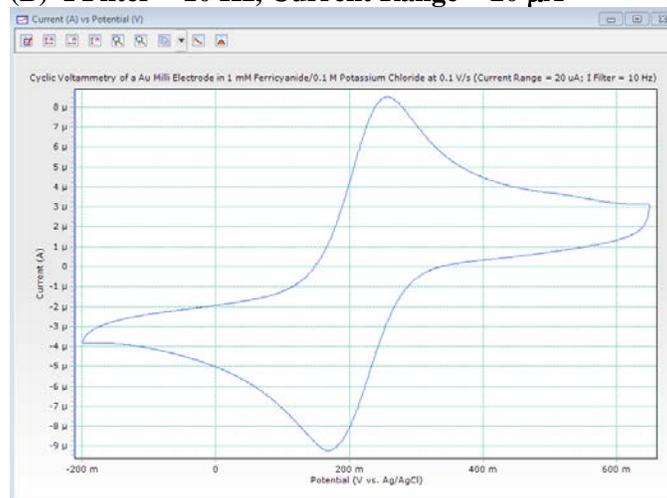
(C)   I Filter = 1 kHz ("Auto"), Current Range = "Auto"
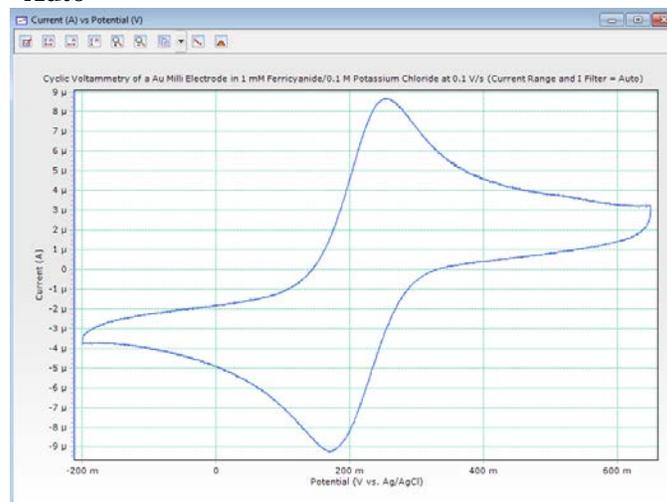

Figure 2: CVs of Au in 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl at ν = 0.1 V/s

spike is a measurement artifact, and is not a spike that occurred at the cell. This is demonstrated in Fig. 5, which is a plot of E versus time for the same CV in Fig. 2 (A) and Fig. 4. Clearly there are no potential spikes corresponding with the current spikes, which verify that the cell was not impacted. Right before the range change, -1.833 μA was measured across a 1 MΩ resistor, resulting in -1.833 mV. The range was quickly changed via fast electronic relays and the next data point should have produced about -0.2 mV for ~2 μA flowing across a 100 kΩ resistor (20 μA range); however, the voltage takes time to adjust from the previous -1.8 mV to the new -0.2 mV. Any data collected during this transition will be obscured and should be considered measurement artifacts. The time taken to regain stability is indicative of the time required for the measured response (i.e. voltage drop across R_m) to pass through the circuitry, which depends on the combined time constants of the circuit. By imposing a 10 Hz I Filter, we have increased the time constant relative to that imposed by the "Auto" setting (1 KHz filter). In this case it takes about 7 data points or 60 ms to regain stability and any data points taken during this transition are invalid.
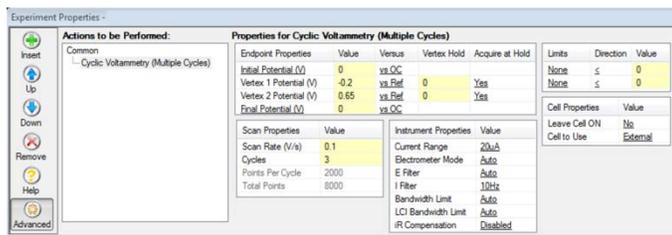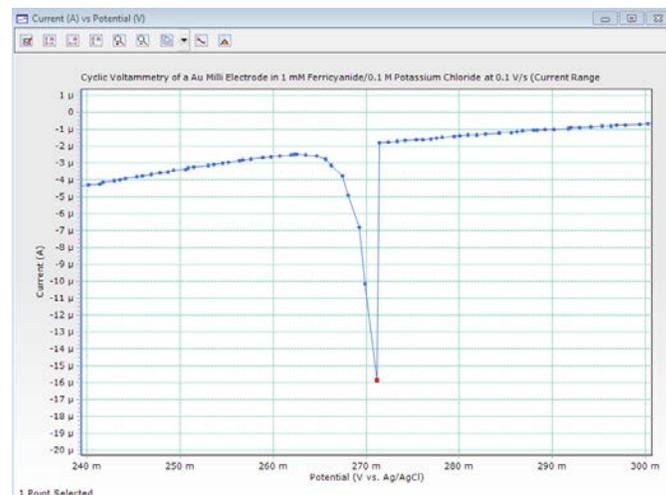

Figure 3: Experiment Properties window

Notice that the spike in Fig. 4 is in the direction of increasing current. This directionality results because the transition is from a smaller to a larger current range (higher value Rm to lower value R_m). On the 2 μA range, -1.833 μA produces -1.833 V. At the instant the range changes, -1.833 V appears across Rm (100 kΩ) for the 20 μA range producing an inaccurately large current reading (-15.865 μA). Thus, the direction of the "spike" (either larger or smaller than the true reading) depends on whether the range change is a range-up or a range-down during the auto range process.

Fig. 2 (B) shows a CV of the same cell collected using a fixed 20 μA range. There are no spikes since the current range does not change. Spikes are also absent from Fig. 2 (C) which was collected using auto current range, but with a faster 1 kHz I Filter. The faster filter results in a

shorter time constant, meaning the measured voltage passes through the circuitry more rapidly.

Figure 4: Close-up view of a spike and the corresponding raw data from CVs plotted in Fig. 2 (A).

The combination of time constants and the sampling rate determine if current spikes are evident in the data. Fig. 6 shows CVs of the same cell taken at 2 V/s with the 1 kHz I Filter, the same filter used in Fig. 2 (C). Current spikes and large sections of overloads (yellow highlighted data) are evident in the CV taken on "Auto" range (blue scan),

which is in contrast to Fig. 2 (C). Since the Cyclic Voltammetry Action collects 2000 points per cycle, the sampling rate (points/s) at 0.1 V/s (Fig. 2 (C)) was 20 times slower than that at 2 V/s. When auto ranging, the faster the sampling rate, the greater the chance that a spike will be captured in the data. As expected, the CV taken with a fixed 200 µA range (red scan) is smooth. These results emphasize that there are time constants inherent to the measurement circuitry even without using the slower 10 Hz I Filter. These are due to the capacitance of the cell combined with the resistance of R_m, for which the time constant increases for larger values (lower ranges). Another factor is the relays themselves, which take milli-seconds to switch. If data are being acquired at micro-second speeds, spikes can occur when auto range is enabled.
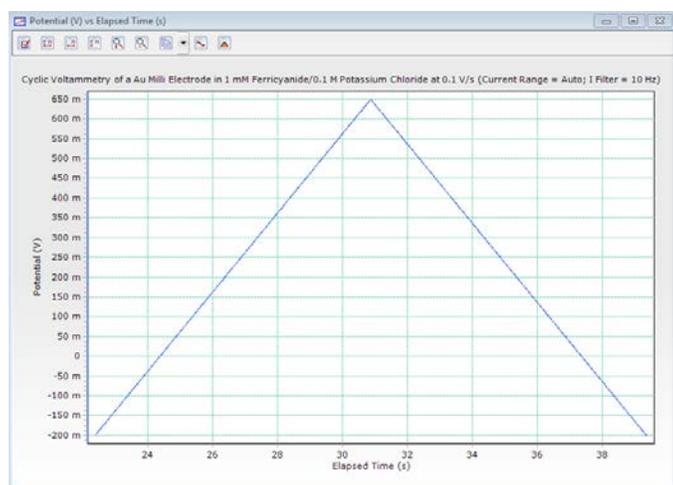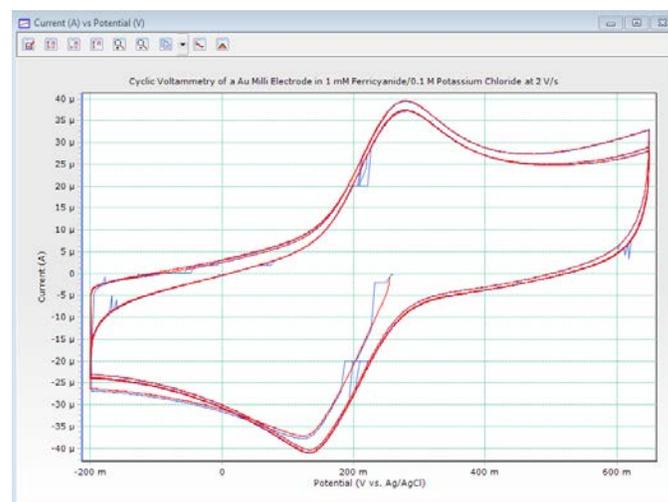

Figure 5: Potential versus time plot for CVs collected on Auto range (Fig. 2 (A)); ν = 2 V/s, I Filter = Auto

Further Considerations

The VersaStudio Manual recommends using a fixed current range if performing fast pulse/step experiments or scans greater than 20 mV/s. This general suggestion, as indicated by the data presented above, is not a hard-fast rule. The maximum scan and pulse/step rates for which auto ranging produces high-quality data is dependent upon the experimental conditions, including the cell's capacitance. Higher capacitance cells are more likely to result in data spikes. The best practice is to use "Auto" range whenever warranted. If spikes and/or overloads occur that disrupt accurate data analysis and/or when "presentation quality" results are required, repeat the experiment on a fixed range, determined by the initial auto ranging experiment, or sample data at a slower rate. For certain high capacitance samples (thick oxide on the

surface of an alloy) spikes will still occur even when using a slow rate. In this situation, it is recommended that the spikes be removed from the data set. This can be accomplished by going to *Data/Delete…/Delete Selected Only or Delete All Overloaded.*

Figure 6: CVs collected on Auto range (blue) and a fixed 200 µA range (red); ν = 2 V/s, I Filter = Auto

There are some cases where auto ranging should always be avoided. These include very fast scans (>1 V/s, i.e. Fig. 6, blue scan) and pulsing or double-step techniques (such as Square Wave Voltammetry or charge measurement Actions), since major gaps in data will occur due to time losses associated with the range change itself.

Special caution should be taken when performing experiments with low input impedance cells such as batteries, fuel cells or super capacitors. A low impedance cell is susceptible to fast changes in current, orders of magnitude in size, with only small changes in potential. The potentiostat is measuring this current and, when set to "Auto" range, attempting to use the appropriate range. Large, fast current changes can lead the hardware to fluctuate between current ranges, causing excessive overloads that produce unnecessary wear on the mechanical and electronic components of the measurement circuit. Therefore, it is recommended that the "Auto" setting be avoided if possible and that all experiments be conducted using the highest current range (2A, for example) first, only switching to lower ranges if deemed appropriate for the experiment. This is a situation where the Auto Current Range Setup Action under the *Advanced Actions* tab can be used to set an initial, minimum and maximum current range. This is achieved by inserting this Advanced Action as a step prior to your experiment Action. A detailed explanation is provided in the VersaStudio manual.