Technical Note

Subject: Best Practices for Improving Tafel Plots of High Capacitance Cells with Low Series Resistance

Date: April 2014

The PARSTAT4000 is designed with both function and versatility at its core. It does not rely on options to provide functionality customized to an application, it is a premier all-in-one potentiostat. The combination of dynamic range and sensitivity provide a differentiated solution to the market and this success is seen in continued growth of the PARSTAT4000 as it continues a proud tradition of potentiostat design.

Different application profiles present different design challenges. Consider, for example, that one potentiostat measures both 4-Amps and fA of current, representing a range of 15 decades of current.

High bandwidth is also designed into every PARSTAT4000. This decision was made early in the design of the instrument to achieve high frequency EIS, fast rise time, etc. We can use other techniques to increase stability with certain applications and cells, but speed has to be engineered into the instrument from the start.

The *Advanced Panel* options provide tools to fit the experiment to the application. There are methods that can be employed even beyond these. This memo describes a specific example where a certain application benefits from methods intended to increase the stability of the potentiostat/cell system. This uses items commonly available in a user's laboratory and does not impact the voltage seen by the cell or the current measured by the system.

It is important to understand that this is not a design fault of the PARSTAT4000. Any potentiostat using an active I-E converter can benefit from a similar approach to decrease noise; it is the extreme bandwidth and extreme low current measurement of the PARSTAT4000 that make it a great candidate for the suggestions in this document.

Application Profile

High bandwidth potentiostats inherently have more noise than low bandwith instruments as noise roughly increases with the square root of the bandwidth. Additionally, the PARSTAT4000 has a hybrid I-E converter. It uses the active I-E converter at the 20 mA range and lower, while the passive I-E converter is used at the 200 mA range and higher. The typical currents observed for a Tafel experiment will require using the active I-E. For all active I-E converters (not just the PARSTAT4000), high capacitance cells with very little series resistance greatly increase the voltage gain of the active I-E converter at certain frequencies, which are related to the range selected and cell used. At low current ranges, this gain increases greatly, amplifies the inherent noise in the instrument and in the cell, and shows up on the resulting data.

Corrosion studies an actively changing sample and gas bubbles are often produced, so noise is commonly attributed to ongoing chemical processes. The currents measured in a typical corrosion experiment, in particular a Tafel experiment, span several current ranges, including the lowest ranges. In addition, highly capacitive cells are often used, due to large sample area and oxide coatings, and the combination of these factors can result in a system that amplifies noise as described previously, and as depicted in **Fig. 1.** Tafel experiments, including that shown in **Fig. 1**, were performed on stainless steel 430 in 0.5 M H_2SO_4 at 0.167 mV/s (1 mV step height, 6 s step time), using a Princeton Applied Research Corrosion Cell Kit (K0047).

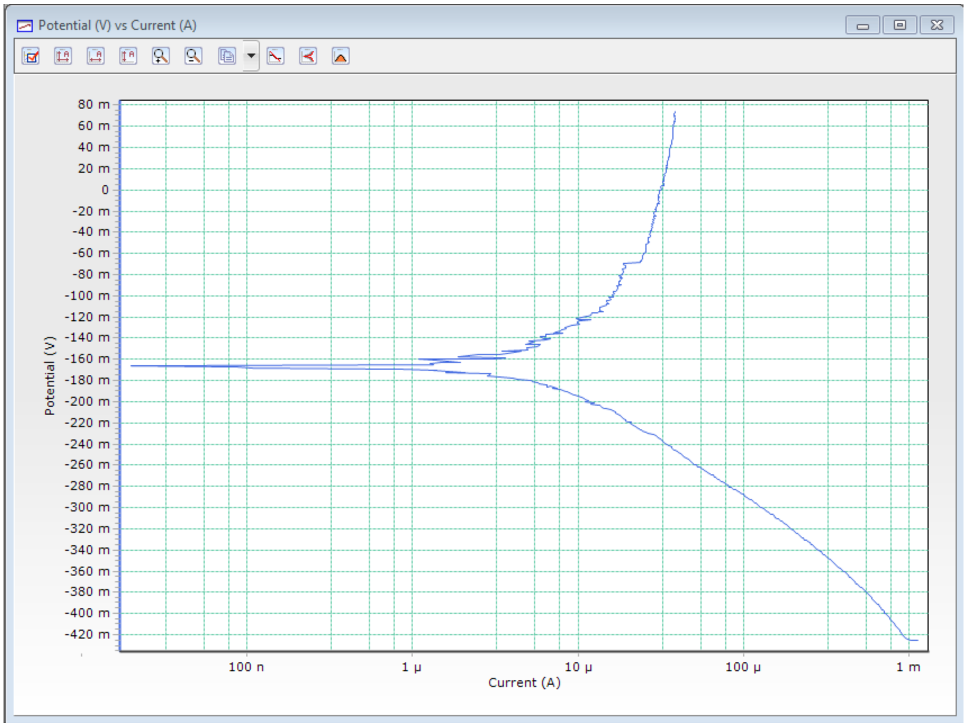

Figure 1: E & I Filters set to Auto (i.e. 10 Hz)

Notice that the noise occurs more and more as the current decreases. Lower instrument current ranges will create higher gain for the noise in the cell and the instrument. When this behavior is first recognized, the *E & I Filters* should be adjusted from "Auto" (i.e. 10 Hz) to 1 Hz and the experiment should be attempted again. **Fig. 2** shows the results obtained with *E & I Filters* set to 1 Hz.

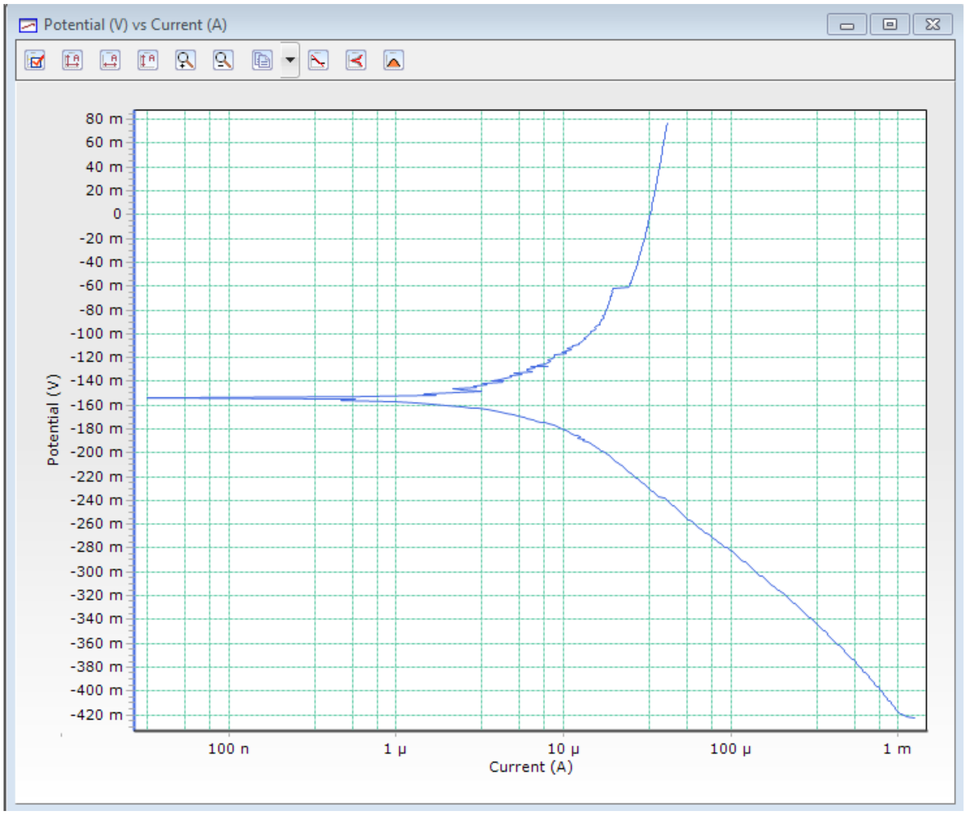

Figure 2: E & I Filters set to 1 Hz

Clearly the noise has been decreased, but not removed entirely. If the 1 Hz filter does not produce satisfactory results, a resistor can be placed in series with the working electrode. This increases the series resistance of the cell, which will reduce the gain of the system over frequencies that cause problems. To maintain the accuracy of the measurement, the sense lead should be connected on the cell side of the resistor as depicted in the graphic in **Fig. 3**. This ensures the resistor is not seen by the Electrometer or the Control Loop in potentiostatic mode.

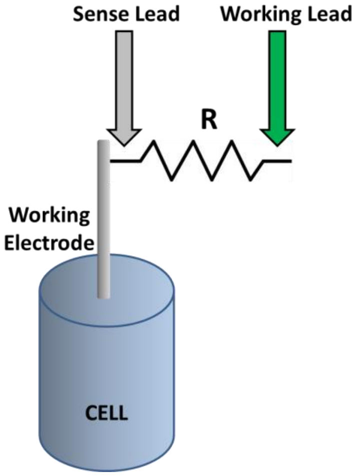

Figure 3: Graphic showing how to connect a resistor in series with the working electrode.

We suggest starting with a small resistor (i.e. ≤ 10 Ω) and increasing the size of the resistor as needed. It is also important that the step time is sufficiently large to allow the system to settle. An appropriate value (in seconds) can be estimated by multiplying the product of the resistor value (in Ohms) and the approximate cell capacitance (in Farads) by 7. **Fig. 4** and **Fig. 5** are Tafel plots of the same cell with a 5.6 Ω resistor in series with the working electrode, using “Auto” and 1 Hz *E & I Filters*, respectively.

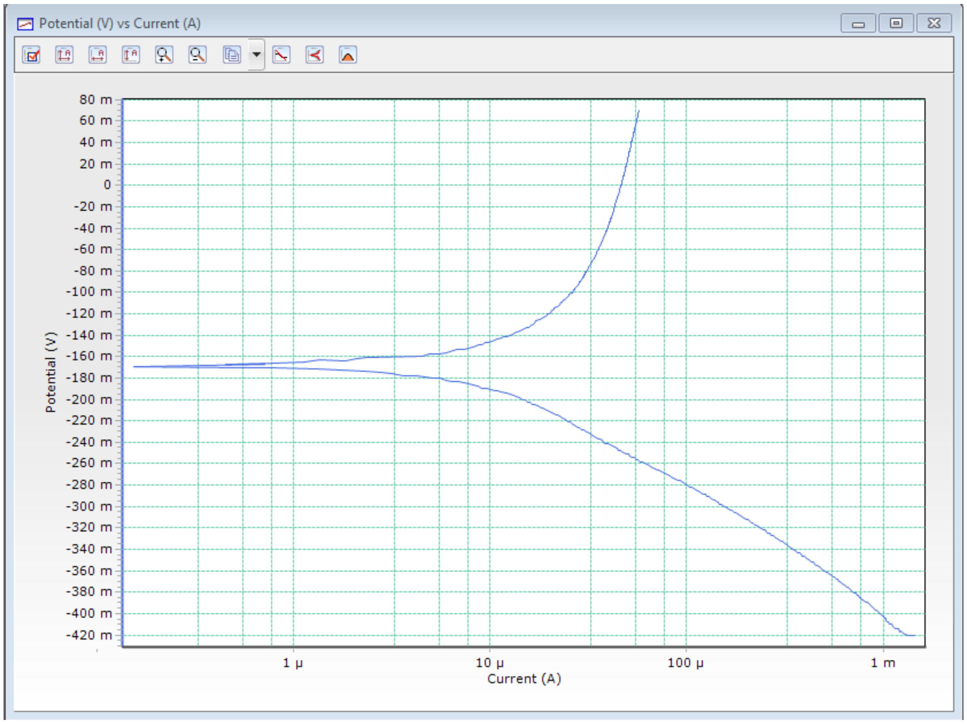

Figure 4: E &I Filters set to Auto (i.e. 10 Hz), 5.6 Ω resistor

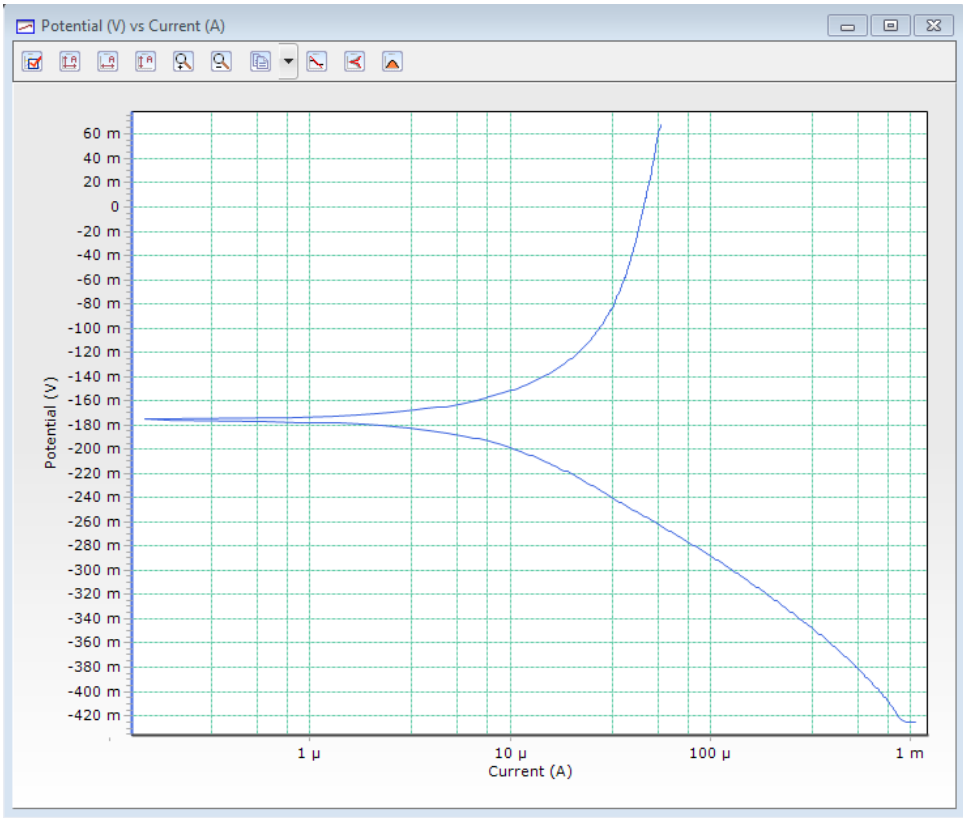

Figure 5: E & I set 1 Hz, 5.6 Ω resistor

Fig. 6 is an overlay of Tafel plots taken with and without the 5.6 Ω resistor using *E & I Filters* set to "Auto" (i.e. **Fig. 1** and **Fig. 4)**. Notice that this graph plots potential versus open circuit on the y-axis, also referred to as Corrosion Potential (E_{CORR}) or overpotential (η), to normalize the data. Clearly, the additional resistor helps to quiet the system, without altering the measurement.

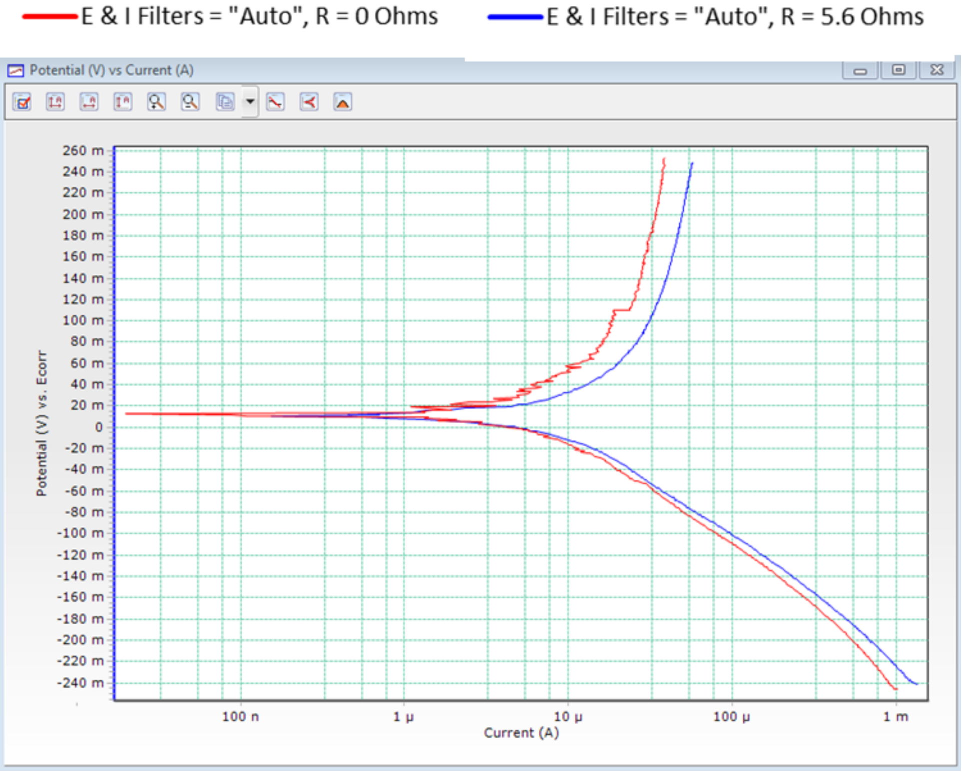

Figure 6: Overlay of Tafel plots collected with the E & I Filters set to "Auto" (i.e. 10 Hz) with and without a 5.6 Ω resistor in series with the working electrode. Note that the overpotential (η), or potential versus the open circuit potential, is plotted on the y-axis. *There is no impact on* E_{CORR} *from this resistor. The small shift in current response is attributed to the non-reproducible nature of the experiment.*

It is critical that the smallest resistor value available, that also reduces noise to an acceptable level, is used. Adding a resistor in series with the cell inevitably increases the RC time constant, thereby slowing down the potentiostat's control loop. If the resistor is large enough for the given experimental conditions, it can result in a lag in the applied potential as seen in Fig. 7, A. This effect is more clearly seen in Fig. 7, B, which shows the non-linearity of the potential vs. time plot for the first ~1400 s.

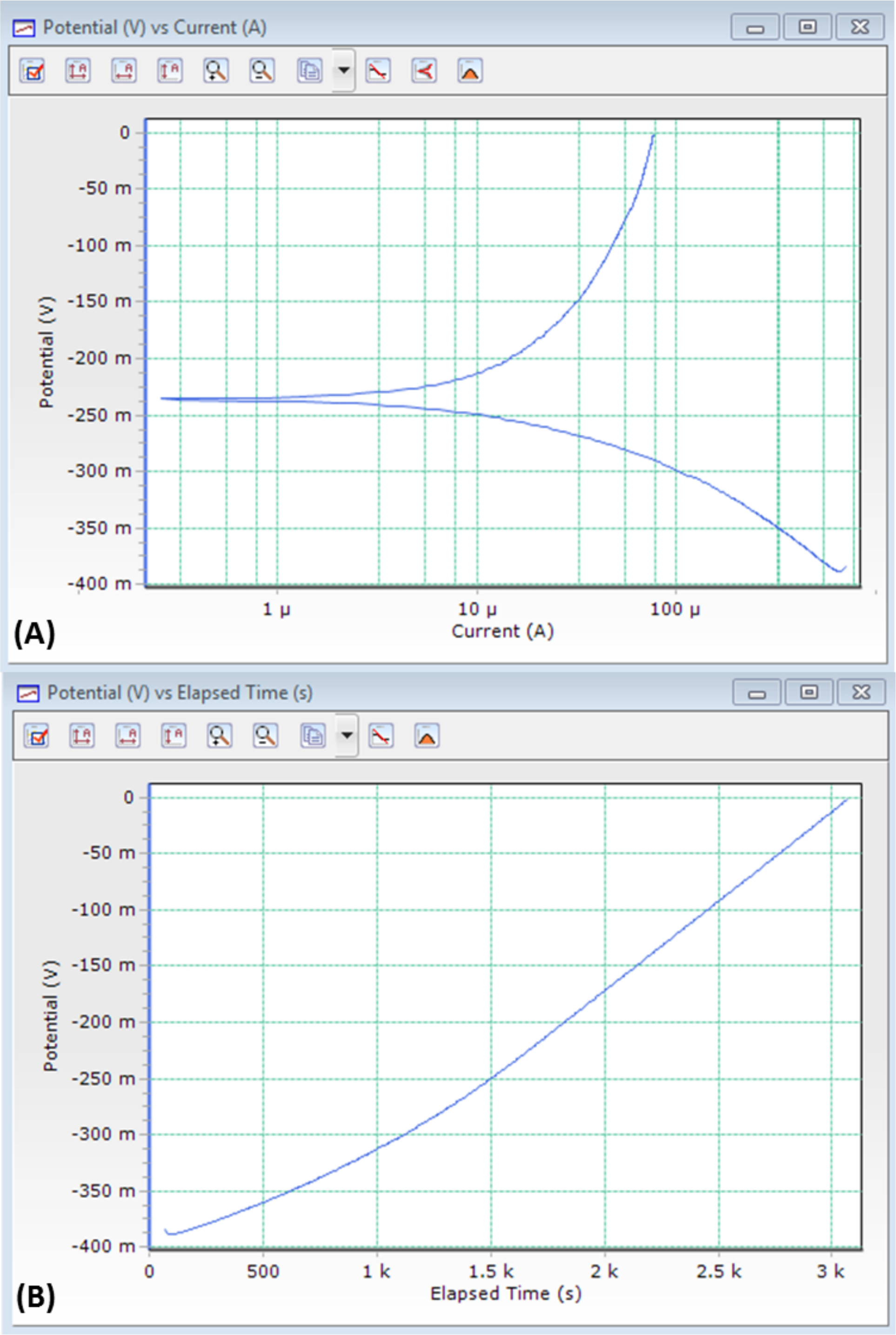

Figure 7: E & I set 1 Hz, 150 Ω resistor

This memo describes an experimental method to increase the stability of a high capacitance/low solution resistance system. Increasing the Filters did improve the data, but with the use of commonly available components, the data became much more stable.

If you have any questions about the content of this Field Memo, please contact Rob Sides, Product Manager, at rob.sides@ametek.com.