Standard Operating Procedure: Spectroelectrochemistry

This technique is carried out in the glove box, so you must be trained on glove box use prior to attempting spec echem. You are required to observe all the rules for glove box use (refer to the appropriate SOP).

Just like for electrochemistry, all the solvents must be purified and properly degassed before using them; $TBAPF_6$ must be recrystallized from ethanol twice. If you're running spec echem on a new molecule, you must run echem first.

Personal Protective Equipment Required

Safety glasses or goggles must be worn when working in the glove box; nitrile or cotton gloves are to be worn under the box's gloves. Long sleeves are strongly recommended, but not required. *Do not wear a lab coat when working in the small glove box*. Nitrile gloves must be worn on top of the box's gloves.

Hazards

There aren't specific risks associated with the use of the potentiostat and/or the spectrophotometer, aside from electric shock.

Working with chemicals can always leads to burns, fires, and other unpleasantness. However, this is a very low-risk experiment. Observe caution as any time you are handling chemicals and flammable solvents.

For risks associated with the use of a glovebox, please refer to that SOP.

Necessary Materials

- Sample (must be dried overnight in a desiccator prior to pumping it into the box)
- Solvent (check to see if there is any in the box)
- Supporting electrolyte ($TBAPF_6$ most of the time; you can use other TBA^+ salts to match your counter anion)
- Working electrode, counter electrode, reference electrode
- Special optical cell
- Vials/pipets (in the box already – if you use them up, you'll have to pump in new ones)

Getting Ready

Pump all necessary materials and compounds into the box.

Turn on the spectrophotometer 30-60 minutes in advance: 1) turn on the switch; 2) open the software (SI 400); 3) when prompted, initialize the system and turn on the UV (deuterium) lamp. **Log your name, the date and time in the log book.**

The potentiostat doesn't need to be warmed up, so you can turn it on at any point before starting the actual experiment.

Sample preparation

Make sure to turn off the catalyst and close the blower before opening any samples/solvents.

Before taking any spectra, you need to blank the SI-400. It's best to take a first blank with an empty sample holder, to identify the offset between the lamps (it is around 400 nm; note its wavelength and magnitude to account for it on your data). The spectrometer will not let you measure any samples until you blank it.

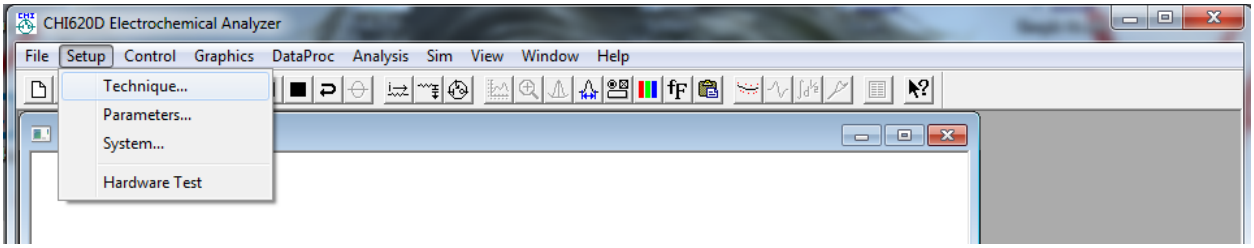
In a vial, prepare 10 mL of a 0.1 M $TBAPF_6$ solution in your solvent of choice (the appropriate amounts are listed on the box) and blank the instrument with it.

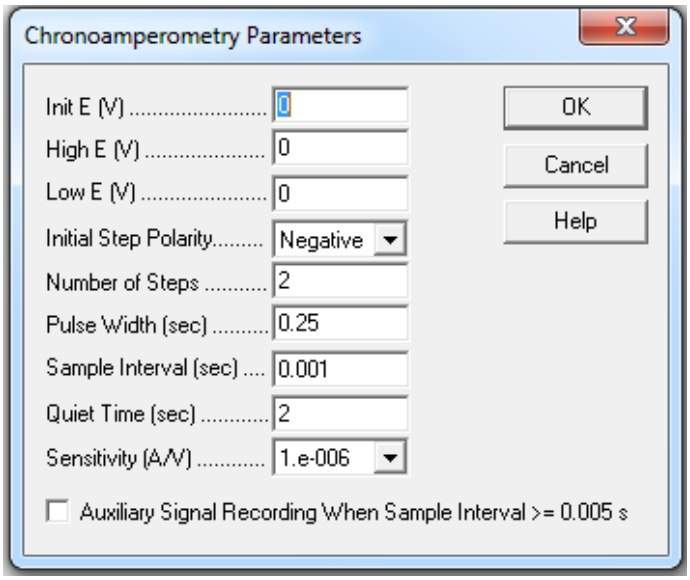
Add enough of your sample to this solution to obtain an absorbance of ~0.4–0.6 at the wavelength of interest (*this is usually the MLCT band*). Save the spectrum of your solution.

Running the experiment

Add the electrodes, setting up the cell so it's ready for the experiment. Take a UV–vis spectrum of the full assembly: this is your "ground state" spectrum (the Pt mesh used as a working electrode contributes to the spectrum, that's why you need this). Save this spectrum as the blank.

In the echem software, on the "technique" menu, select CHRONOAMPEROMETRY.



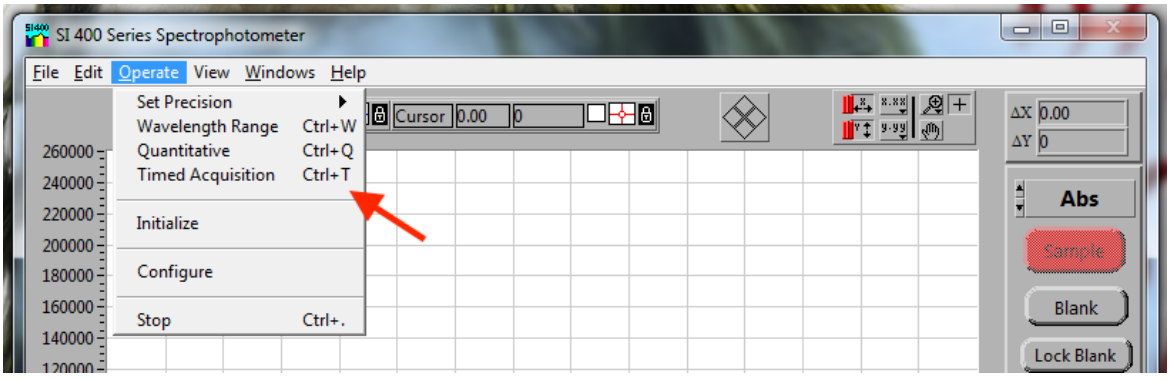


Settings:

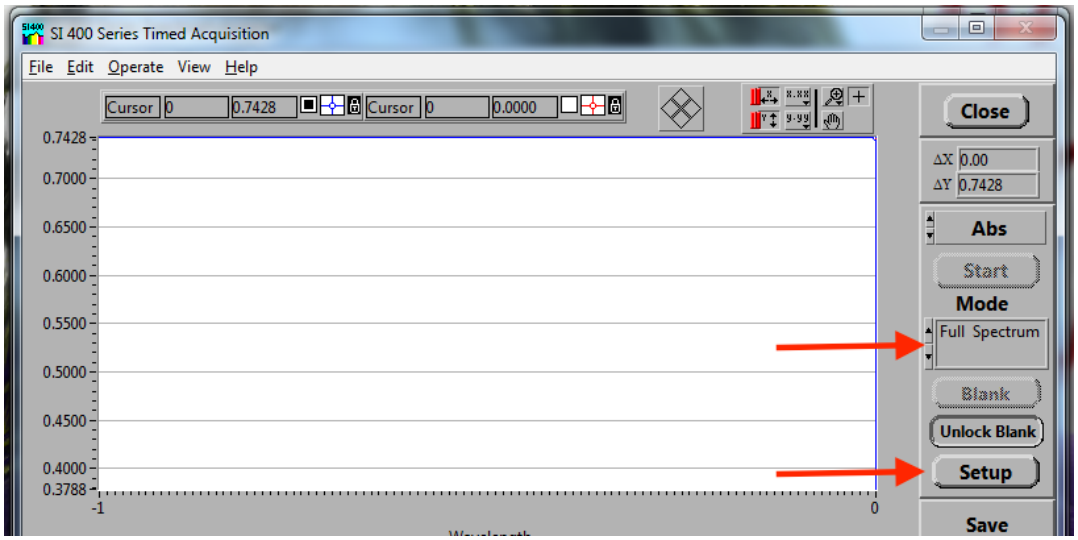
Initial E	High/Low E	Steps	Pulse Width	Sample Interval	Quiet Time	Sensitivity
See below	Your initial value ± 0.01 V	1	1000 s	0.1 s	2 s	10^{-5} A/V

The initial voltage must be ~100 mV more reducing or oxidizing than $E_{½}$ for your molecule. This value is with respect to our echem reference electrode, not vs. ferrocene. You might have to adjust this potential while running (you can stop the echem at any time).

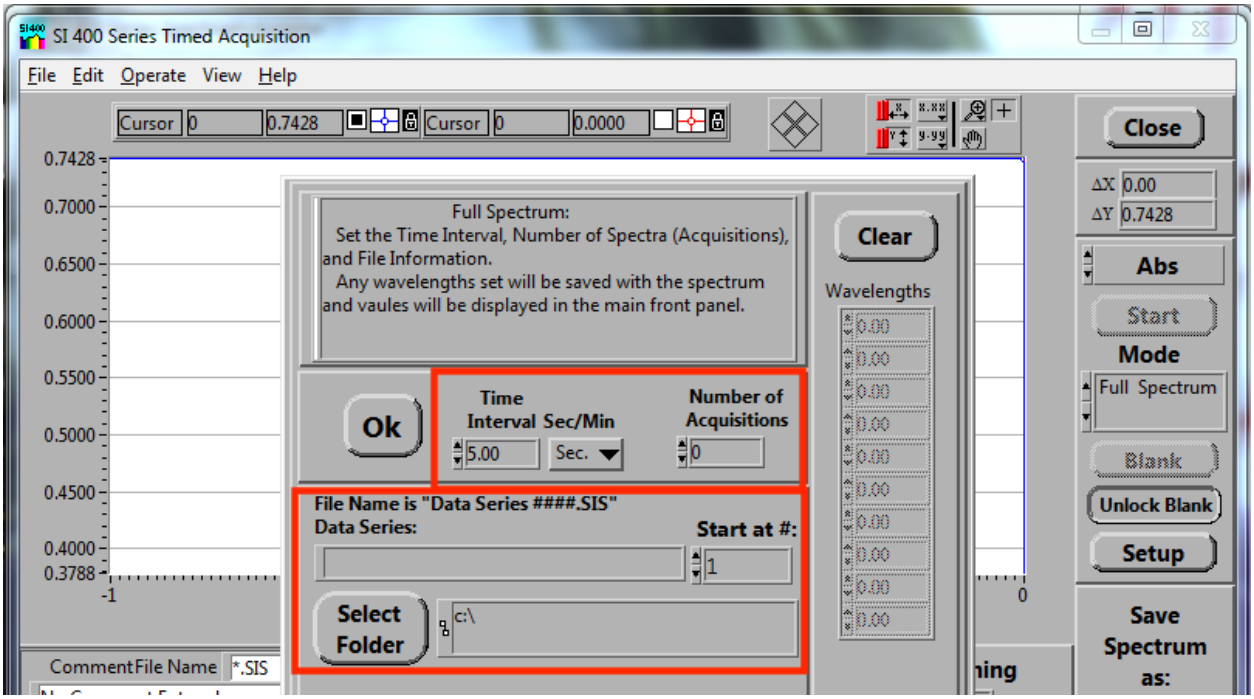
In the spectrometer software, go to the TIMED ACQUISITION menu:



Once in the Timed Acquisition window, make sure that the "full spectrum" mode is selected. Open the setup menu:



Select a 30 second time interval and 21 acquisitions. Choose a name for the file (it will be saved as a csv-type) and the folder where you want to save your data.



Make sure you've blanked the spectrometer with your sample + electrodes. Then start the timed acquisition. After taking one spectrum without applied potential, start the chronoamperometry. You're running!

Things to keep an eye on while collecting data: 1) if the potentiostat overflows, stop the run and decrease the sensitivity, then run it again; 2) your spectra should keep changing: if they

remain the same or the changes decrease, stop the echem run and make the potential more reducing/oxidizing. You don't need to stop the timed acquisition when doing any of these.

Once the timed acquisition is done, discard the solution, replace it with fresh solution and repeat the procedure. It is best to collect duplicates or triplicates of the data.

When you turn off the SI-400, **don't forget to complete the log book.**

If the spectrophotometer crashes: close all the programs, open the SI 400 software again, initialize it and turn the UV lamp back on. Let it stabilize for ~20 min before collecting data again.

Final Clean-up

When you are done, collect all trash/waste and take them out of the box to be properly disposed. Wipe the bottom of the floor with a paper towel and some solvent and clean any spills. Make sure to purge the box for 30 minutes, and then open the catalyst and turn the blower back on.

For the electrodes: wipe the counter electrode with a kimwipe and solvent; the same goes for the working electrode (you might have to dip it in solvent instead). Then have the counter and working electrodes soak for one hour in 1M HNO_3, rinse them with DI water and let them air dry. The counter electrode must be soaked in 1M HNO_3 for an hour, then rinsed with DI water and stored in its 3M NaCl solution.

Last Updated: April 2017 – DAR