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Using Cyclic-Step Chronopotentiometry to Explore Electron Mobility in Dye-Sensitized Solar Cells

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Introduction

In recent years there have been studies done to create more cost-effective ways to capture solar energy. As a result, dye-sensitized solar cells were created and researched as a possible alternative for traditional silicon solar panels.[1] For the purposes of this experiment, devices were made using titanium dioxide (TiO_2) with the anthocyanin dye from raspberries. This kind of device uses lower cost materials compared to commercial devices but has much to be desired in efficiency.[2] The devices that were used in this experiment used electron transfer from the photoexcited chromophores to the TiO_2 in the devices.[3] The incomplete electron transfer process is theorized to be caused by injection into trap states making it difficult for the electron to leave the trap states and thus preventing future injection events.[2]

In this experiment, electrolyte solutions were tested: one that contained lithium and one that without lithium. It has been shown that lithium can intercalate into the lattice structure of the titanium dioxide.[4] Through intercalation the lithium causes the acceptor state to become lower in energy which increases the rate of electron injection.[2]

In addition to lithium electrolytes being used, this experiment utilizes raspberry dye. This approach has the advantage of being green in the sense that the dye is made from natural material and is eco-friendly compared to other dyes using heavy metals.[2] Overall this experiment aims to further understand the ability of lithium to lower the energy of the conduction band by adding it to the electrolyte solution. While other works in the past have applied a current over time the work in this experiment will be measuring an applied potential over time.[2]

Methods[2]

The paste for the dye-sensitized solar cells was made by mixing about 0.5 grams of TiO_2 and 1.5 milliliters of acetic acid. A few drops of detergent were added to the mixture. On the conductive side a clear tape stencil was applied in a way that allowed for a small rectangle at the end of the slide to not be covered by tape. The TiO_2 paste was applied to the uncovered

area the stencil removed allowed to air dry and placed in the oven for an hour at 350^{o}C. The oven was turned off and the glass slides allowed to cool for 24 hours.

Raspberry dye was made by crushing 7 raspberries into a paste in a mortar. The isopropyl alcohol (10 mL) was added to the raspberry paste. The results paste mixture was filtered using a Buchner funnel.

The lithium electrolyte solution was made by mixing iodine (0.1008 g or 0.7943 mmol), potassium iodide (0.8352 g or 5.0312 mmol), ethylene glycol (10 mL), and lithium perchlorate (0.1191 g or 1.1195 mmol). The electrolyte solution without lithium was made by mixing iodine (0.1092 g or 0.8605 mmol), potassium iodide (0.8426 g or 5.0758 mmol), and ethylene glycol (10 mL).

A few drops of raspberry dye were added to the TiO_2 paste on the glass slides and allowed to sit for no less than three minutes. A soot layer was applied to the conductive side of another slide by placing it under a flame and moving it across a candle flame. The slides with paste and dye were rinsed gently with water and ethanol and allowed to air dry. The slides with soot were wiped of extra soot so the soot area matched the paste area. Slides were prepared by adding with a few drops of solution with or without lithium, respectively. These slides were then matched with a soot applied slide to complete the dye-sensitized solar cell.

The solar cells had the current tested with chronoampermetry using the Pine Wavenow Potentiostat. The setup used for the test utilized the default parameters for the first set of parameters and the second set to 0 volts and 60 seconds, no auto range, and 6000 intervals. A light, from a plug in lamp, was shined on and off the device. The current in µA was recorded.

For the one-minute trials, the slides were tested, with devices under dark conditions for 10 minutes before testing depending on the trial conditions, with cyclic step chronopotentiometry. The setup was with two steps and five interactions. Step one was done at 0 µA for 60 seconds with 6000 intervals. Step two was done at the recorded µA from the current test for 60 seconds with 6000 intervals. The auto range was turned off. While testing the devices

were kept under dark conditions. For the two-minute trials, the same setup as the one-minute trials was done except all with 120 seconds and 12000 intervals.

The data from the trials other than the current test was placed into a script in RStudio that read the data and found the decay (Figure 1). The starting coefficients and placement to

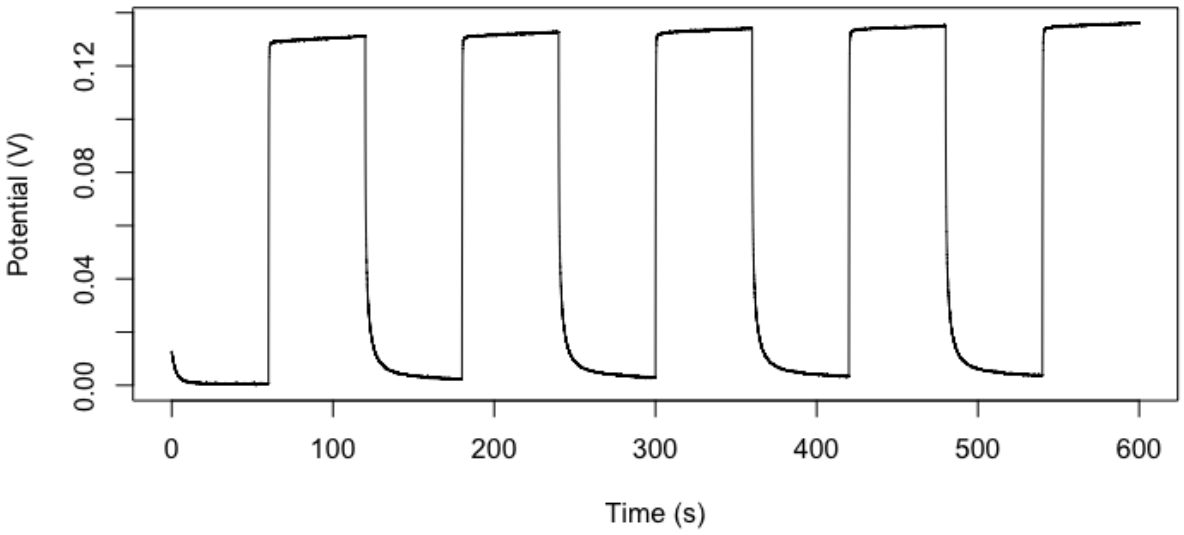

***Figure 1**. "With Li 1 Minute at 50 µA at 6000 Intervals after 10 Minutes in Dark Trial"* A raw data example for the on/off-cycle

find the decays were altered slightly depending on the trial. The decay data was normalized, where the data points were divided by the highest value at time zero, so the different curves could be compared. The code then put all decays found into an exponential decay curve of best fit (Equation 1) and found the coefficients a, b, c, j, k, and l for the best-fit curve.

$$y = ae^{-(\frac{t}{j})} + be^{-(\frac{t}{k})} + ce^{-(\frac{t}{l})} \quad (1)$$

The coefficients a, b, and c are the relative population for each lifetime with a being the relative population of the fastest lifetime, b being the intermediate speed, and c being the slowest. The coefficients j, k, and l are the lifetime in seconds from fastest to slowest. The terms y is the potential and t is time in seconds. The coefficients a, b, c, j, k, and l were compared.

Discussion

The decay fit equation that was used for this experiment was a tri-exponential decay. A tri-exponential decay was used because when fitting the graphs with a bi-exponential decay did not match the collected data well. This differs from the tri-exponential decay fits which matched the data well (Figure 2). The coefficients, a, b, and c, the sum should equal 1, because the data

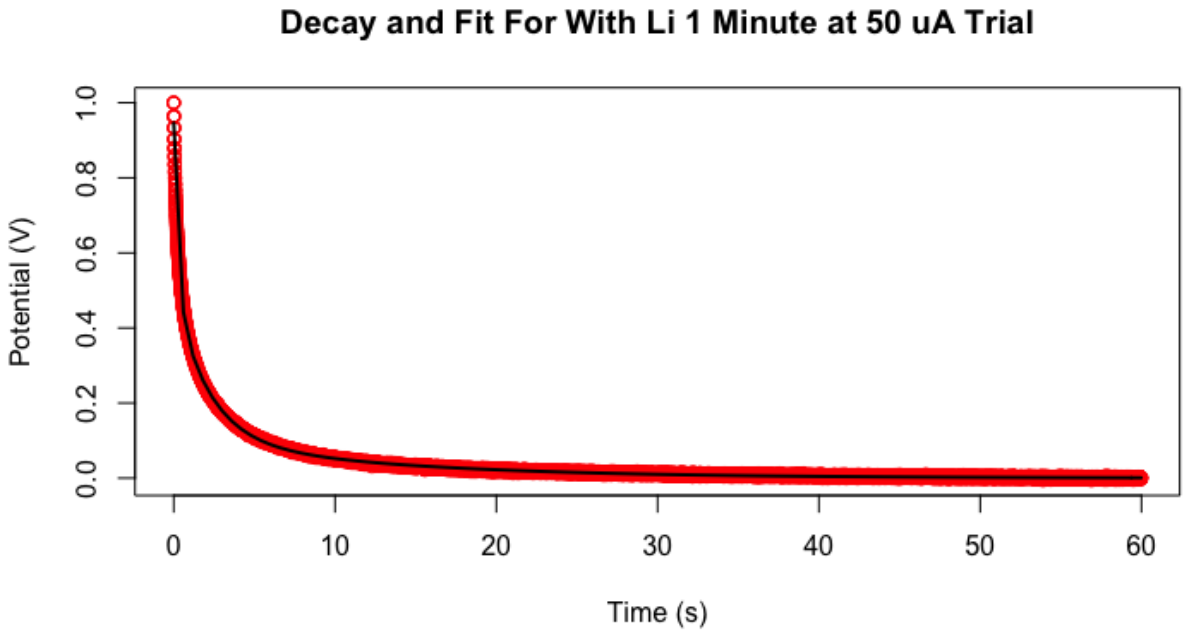

Figure 2. *"Decay and Fit for with Li 1 Minute at 50 µA Trial" A decay curve of the four combined decays of one device with the exponential fit*

was normalized, however the data shows that the sum is around 0.9 which is explained by the fact that the data in the experiment had error and so to account for the error the fit was allowed to not equal 1. This experiment only focused on dark conditions for all trials. The reason behind this was to prevent the light from adding variables that would complicate the experiment. From the graphs there is no significant difference between with and without Li and the 25 µA and 50 µA. This was unexpected since previous studies had indicated a significant difference between devices that contained lithium versus those that didn't contain lithium.[2,4] There was a significant difference between the 1-minute and 2-minute trials which was seen by the lack of overlap

between the 1 and 2-minute trials (Figure 3). When the l, k, and j values of the 1-minute trials

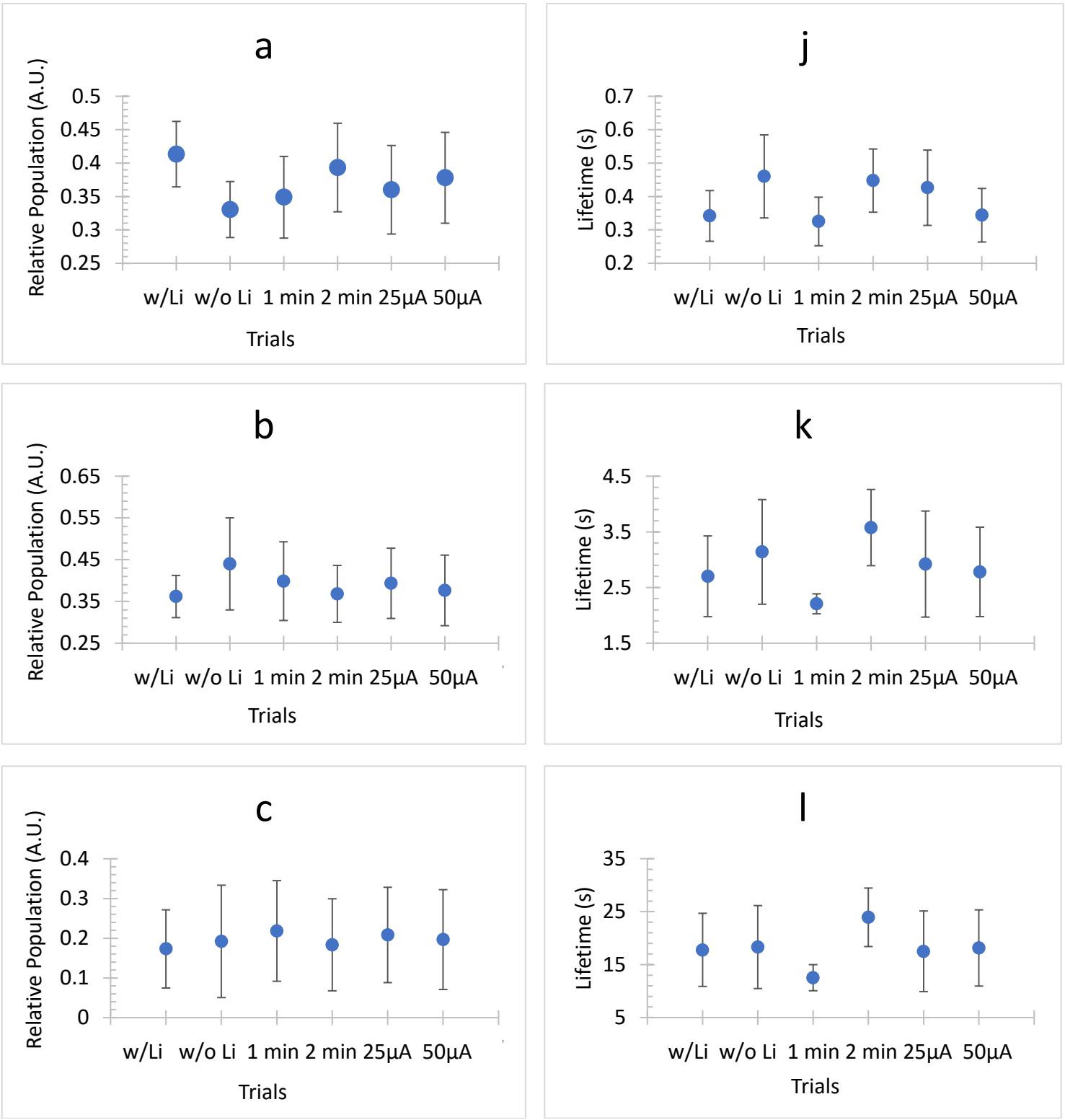

Figure 3. *The average and errors comparing the different trials for the different coefficients of the tri-exponential decay.*

had a lower lifetime than those of the 2-minute trials. The results suggest that the electrons in

the 1-minute trials are able to escape the system faster than the 2-minute trials and is interesting due to the fact that the electrons can enter the system within picoseconds while they leave within minutes.[1,3] Our results then suggest that compared to excited electrons entering the system, the electrons stay in the system significantly longer. Causing the excited electrons to be unable to be injected due to the filled acceptor states. This demonstrates an inefficiency issue in dye-sensitized solar cells. Currently there is no explanation of the trend between 1 and 2-minute trials. However, there are two hypotheses: the first hypothesis is that the 1-minute trials happen so quickly that the electrons are unable to fully leave before the next on-cycle. Meanwhile the 2-minute trials are long enough to allow the electrons to fully leave the system. The second hypothesis is the 2-minute on-cycle is long enough for all the trap states to be filled while the 1-minute trial is unable to completely fill all the trap states.

Conclusion

The experiment showed no significant difference between all the trials except the 1-minute versus 2-minute trials. The differences in the 1-minute versus 2-minute trials show an inefficiency of the dye-sensitized solar cell devices used in the experiment. This is due to the fact that electron injection can occur on the picosecond timescale, but our data suggests that electrons can possibly persist on the minute timescale.[1,3] Most solutions for the inefficiencies have focused on the picosecond timescale and have ignored the possible inefficiencies that could occur long-term. In order to explain this trend, there are two current theories on how the difference came about. Further exploration into the difference between 1-minute and 2-minute trials provides a potential area for future research to better dye-sensitized solar cells. In addition, an exploration into the reason behind the trend could prove beneficial.

References

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