Methanol Cyclic Voltammetric Observations

Over the past few weeks, I have been analyzing data, which I collected earlier in the semester. Here are some highlights, pertaining to methanol experiments, which were intended to characterize the parc potentiostat and calomel reference electrode...

Figure 1: Represents the highest concentration of sulfuric acid and methanol achievable without inducing an overcurrent measurement. For this and all subsequent data sets, the ratio of sulfuric acid to methanol was kept 1:1 on a molar concentration basis, since the literature seemed to adhere to this rule of thumb. Notice that sulfuric acid alone produces an oxidation and reduction peak, roughly 0.90 V and 0.52 V, respectively, which has to be taken into account when evaluating methanol oxidation peaks. Originally, I thought that this might be due to contamination, because I never observed this pair at higher solute concentrations.

Figure 2: My first curiosity was to determine which scanrate would best suit the methanol oxidation peaks. Since scanrates higher than 25 mV/s started to reveal other oxidation peaks and amplified the sulfuric acid peak at the expense of methanol oxidation, I settled on 25 mV/s as a first approximation.

Figure 3: For further confirmation of the 25 mV/s choice, I looked at how the peaks changed as the number of cycles increased. For 25 mV/s, the methanol oxidation peaks enhanced with each cycle.

Figure 4: In contrast, bumping up the scanrate to 50 mV/s actually dimished the methanol oxidation peaks as the number of cycles increased, characteristic of a mass transport limited situation. Notice for both figures 3 and 4, the sulfuric acid peaks exhibit no change with cycles regardless of scanrate.

Figure 5: Perhaps the most exciting and unexpected results appear in this data set. Decreasing solute concentrations revealed significant methanol oxidation peak enhancement, as if each run had a cumulative effect to activate the Pt catalyst. All these data sets were run on the same day with fresh solutions, from highest to lowest solute concentration; however, the electrodes were just soaked and rinsed with deionized water in between runs.

Figure 6: Although methanol was present in these runs, the Pt wire working electrode had not been properly activated, so no methanol oxidation peaks appear. The comparison between these two scans demonstrates that you can remove the presence of the sulfuric acid oxidation/ reduction peaks by changing the voltage range. Also, the sulfuric acid peaks do not depend on catalytic activation as dramatically as methanol.

Figure 7:   After determining better run conditions for achieving methanol oxidation, I decided to revisit scanrate optimization, reducing the scanrate below the benchmark 25 mV/s level. This was the first run of the day, with the Pt electrode having no prior run history. As the data suggests, lowering the scanrate may not give the Pt electrode the necessary current for activation. In fact, the methanol oxidation peaks diminished from 1st to 10th cycle, characteristic of a diffusion limited case.

Figure 8:   Both of these runs were done under the exact same experimental conditions, except the electrodes had a different run history... the tale of two electrodes. This underscores the necessity for electrode activation in the methanol system. The purple curve came from figure 5, where it had gone from high to low solute concentration; whereas, the green curve had stayed at the same concentration, but only had the scanrate increased from 5 to 25 mV/s.

Although I don't know the exact process which activates the catalyst, I did stumble upon a recipe which achieves activation. Within the literature, people generally dwell at a particular voltage for a specific length of time to attain electrocatalytic activation. However, these experiments did fall within the boundaries of the objectives I had hoped to accomplish. Clearly, the low current, parc pontentiostat works far better than a normal current, model 273, and should give us the sensitivity needed for ruthenium based ECL. Additionally, if you take the voltage measurements where methanol oxidation occurs at a decade in concentration apart, a comparison between figures 1 and 5, then extrapolate those voltages up to 500 mM, the values commonly reported in the literature, the two methanol oxidation peaks occur at roughly 0.64 and 0.43 V, which validates the instrument and calomel calibration. If I were to continue work from here, I would take the Pt and glassy carbon electrodes and do some static CV's to determine the optimum conditions to make $Ru(bipy)_3^{+1}$. From there, I could launch into rotating electrode measurements to elucidate the lifetime values.

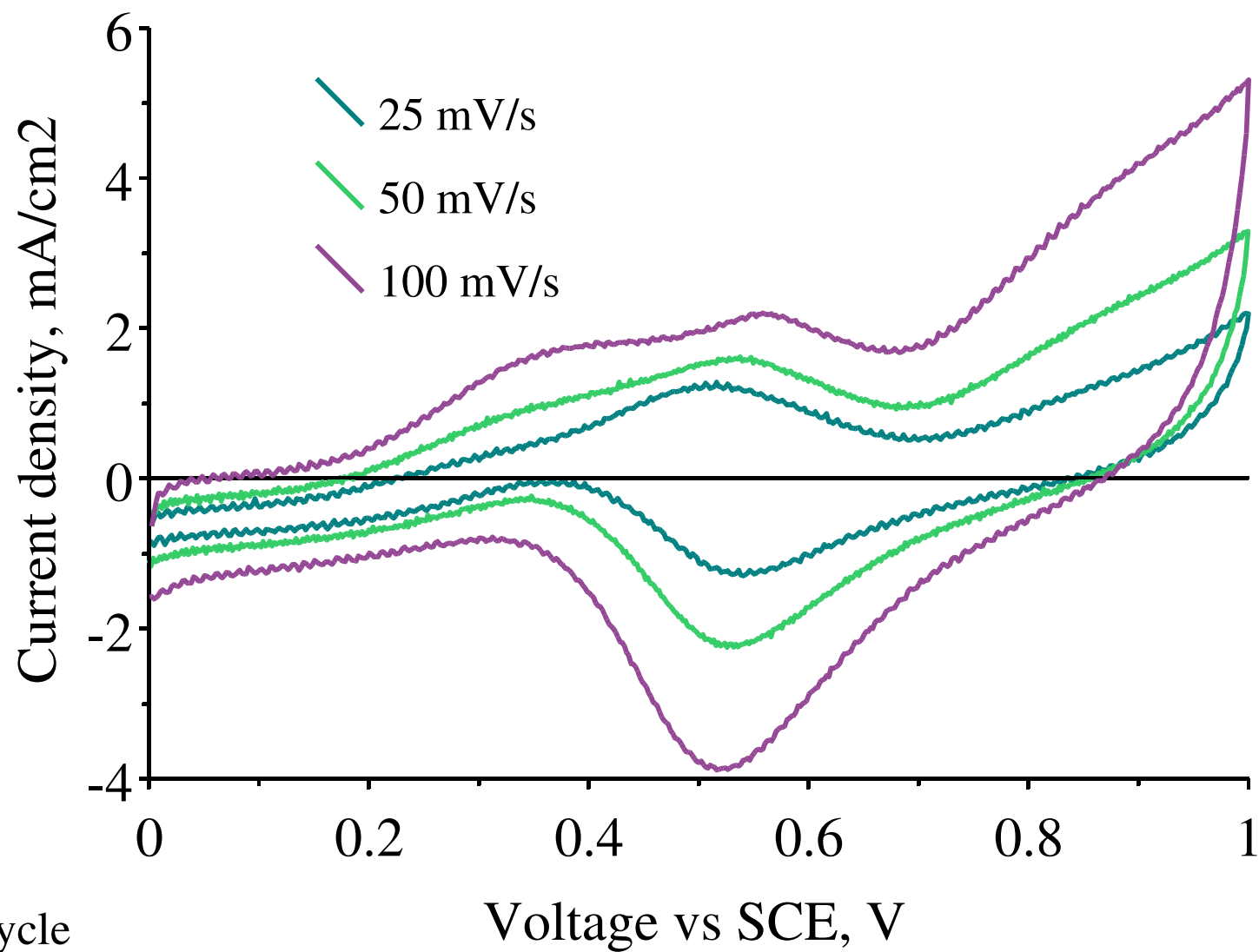Figure 1: Highest Attainable Solute Concentrations

- 50 mM H2SO4
- 50 mM H2SO4 + 50 mM MeOH

Current density, mA/cm2

Voltage vs SCE, V
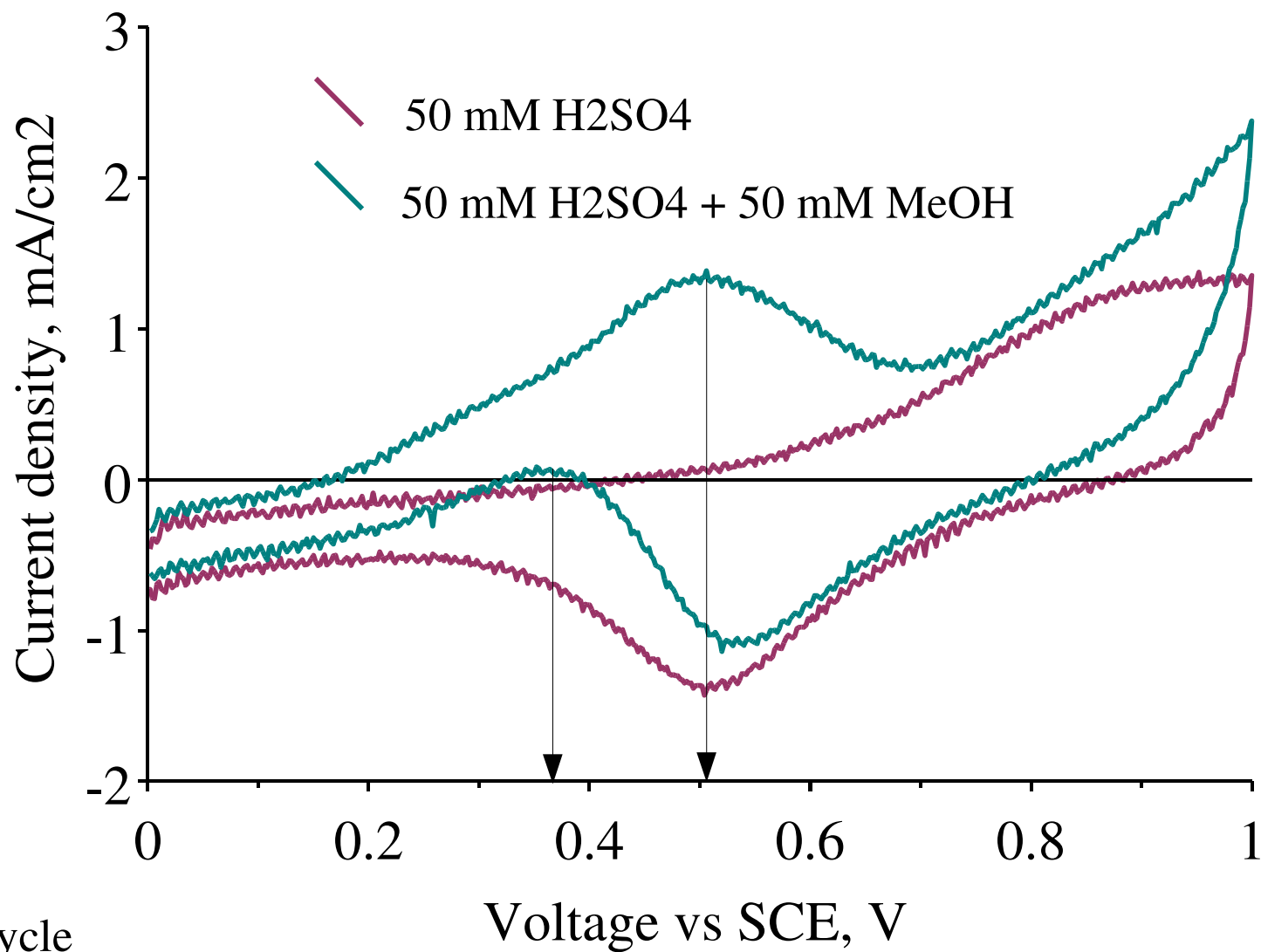
10th cycle

Pt wire electrode

25 mV/s scanrate

Figure 2: Influence of Scanrate on MeOH Oxidation Peaks

25 mV/s
50 mV/s
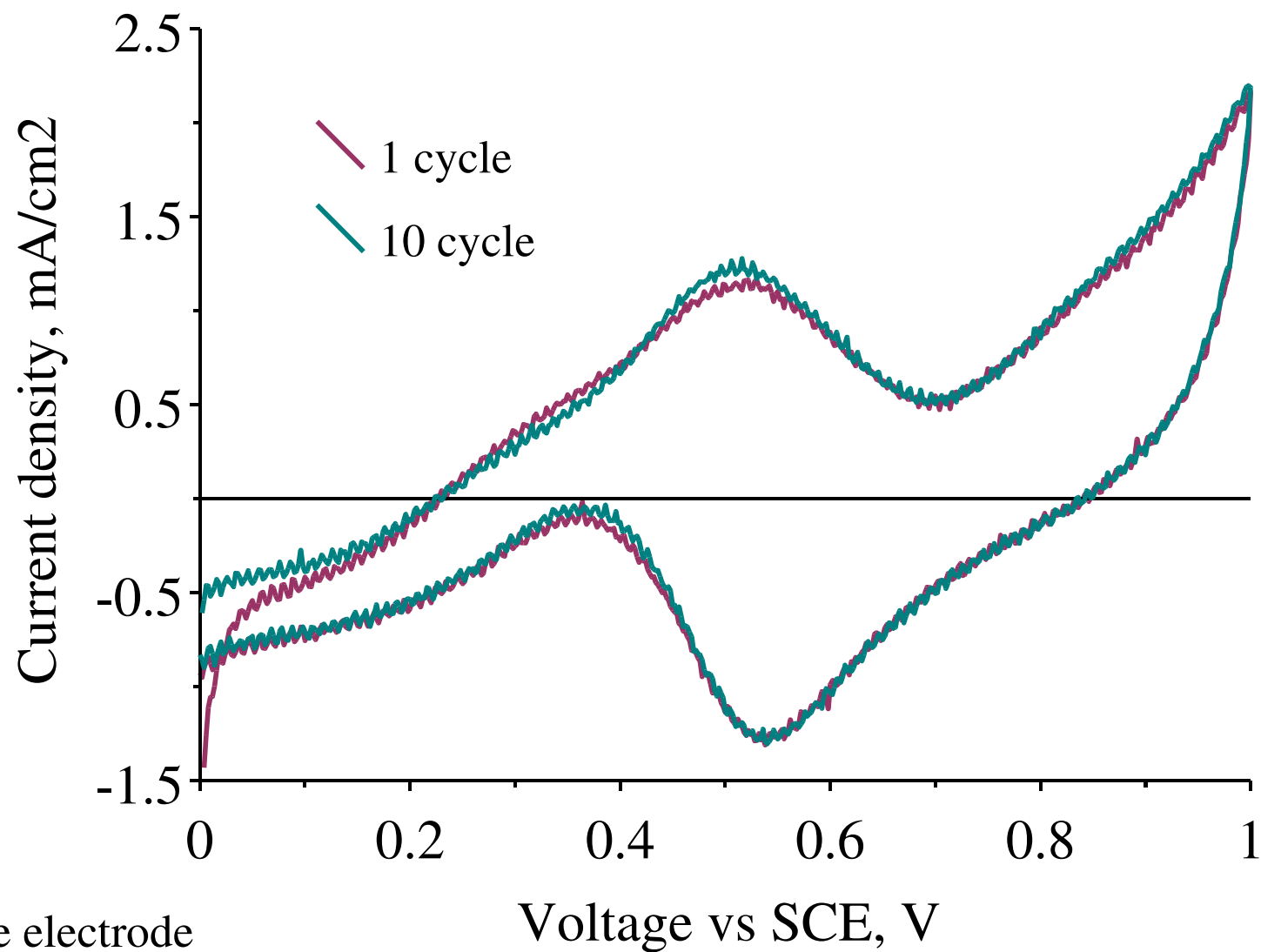100 mV/s

Current density, mA/cm2

Voltage vs SCE, V

10th cycle

Pt wire electrode

50 mM H2SO4 + 50 mM MeOH

Figure 3: Evolution of MeOH Oxidation Peaks

Pt wire electrode

25 mV/s scanrate

50 mM H2SO4 + 50 mM MeOH

Figure 4: Turning Point for MeOH Oxidation Peaks
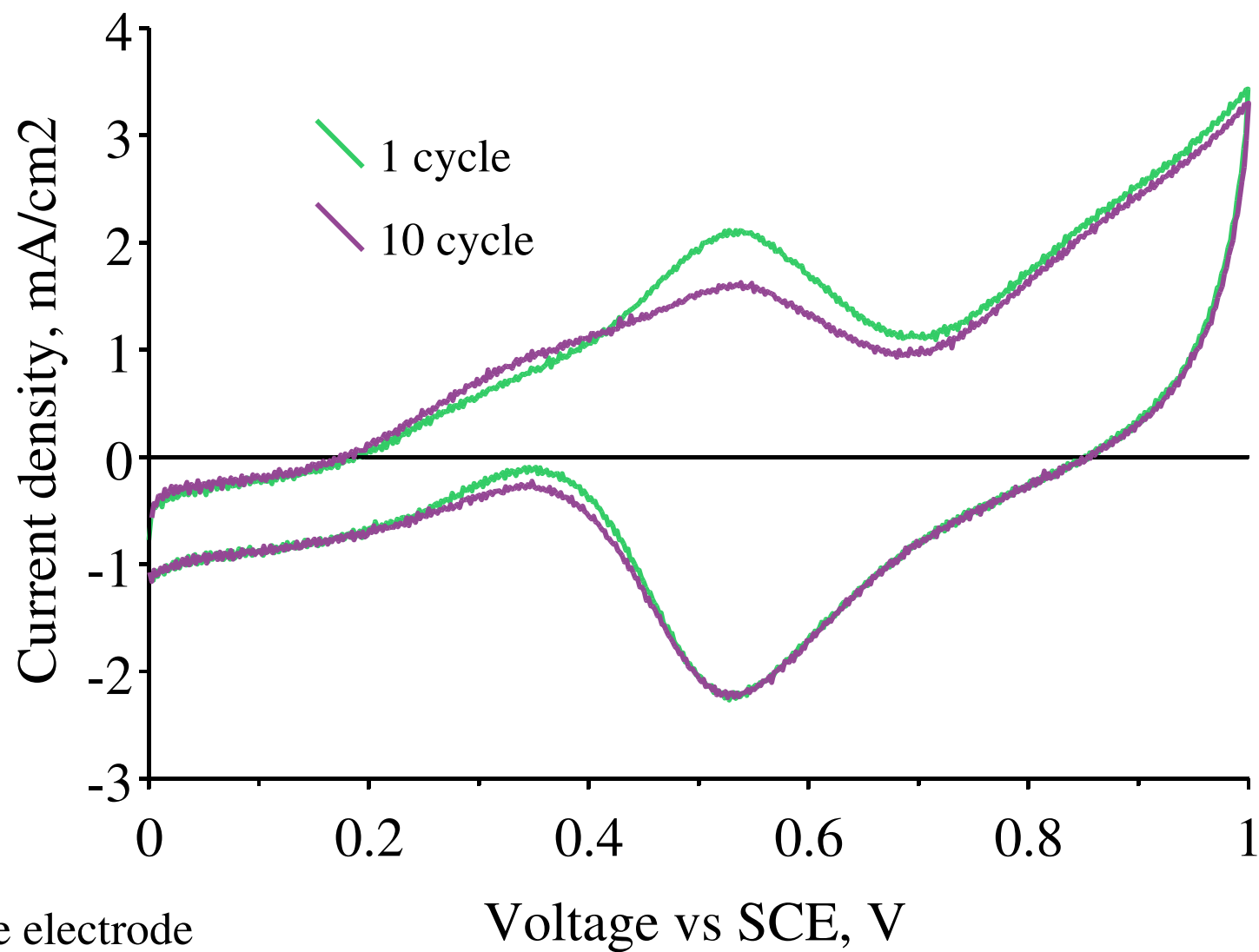
Pt wire electrode

50 mV/s scanrate

50 mM H2SO4 + 50 mM MeOH

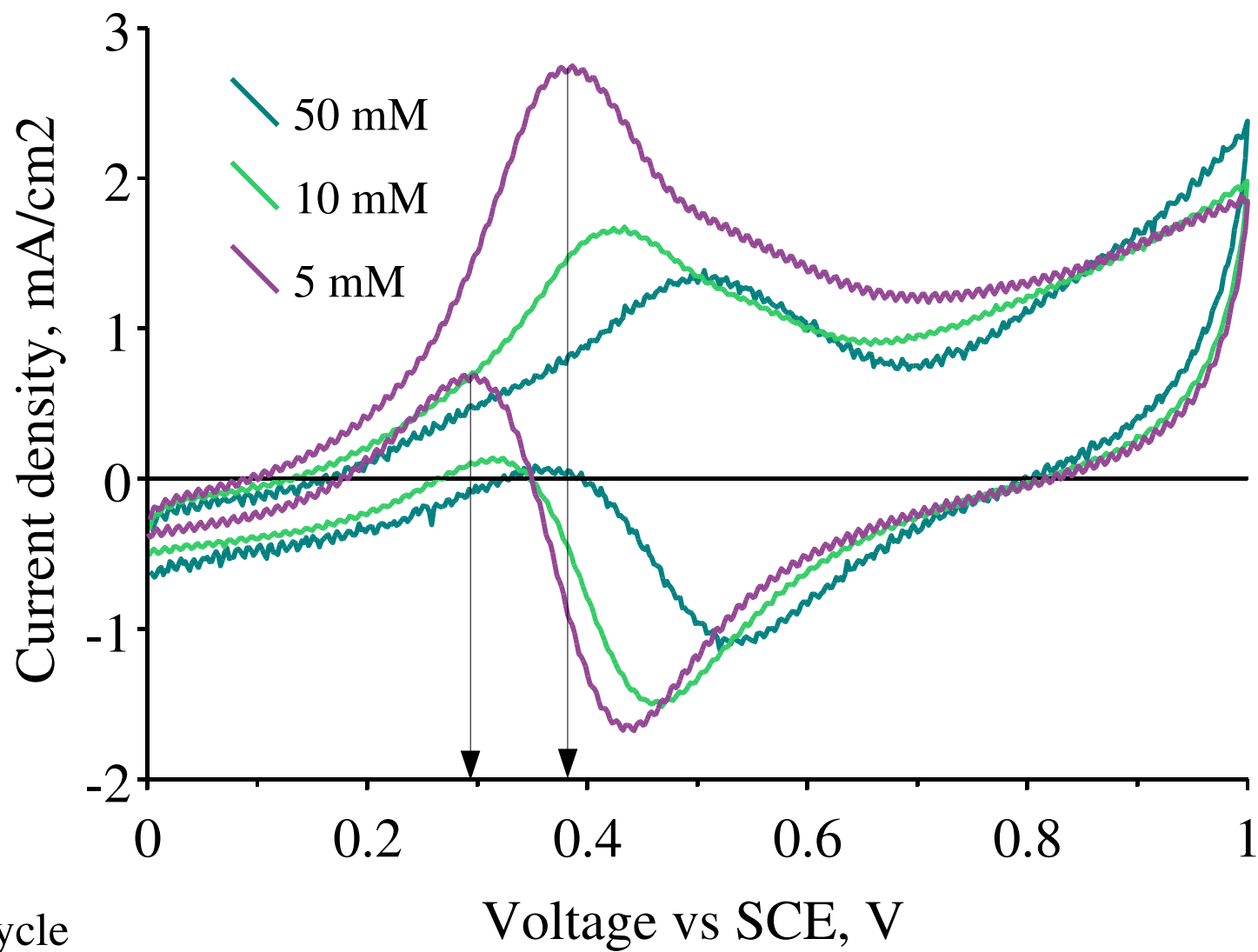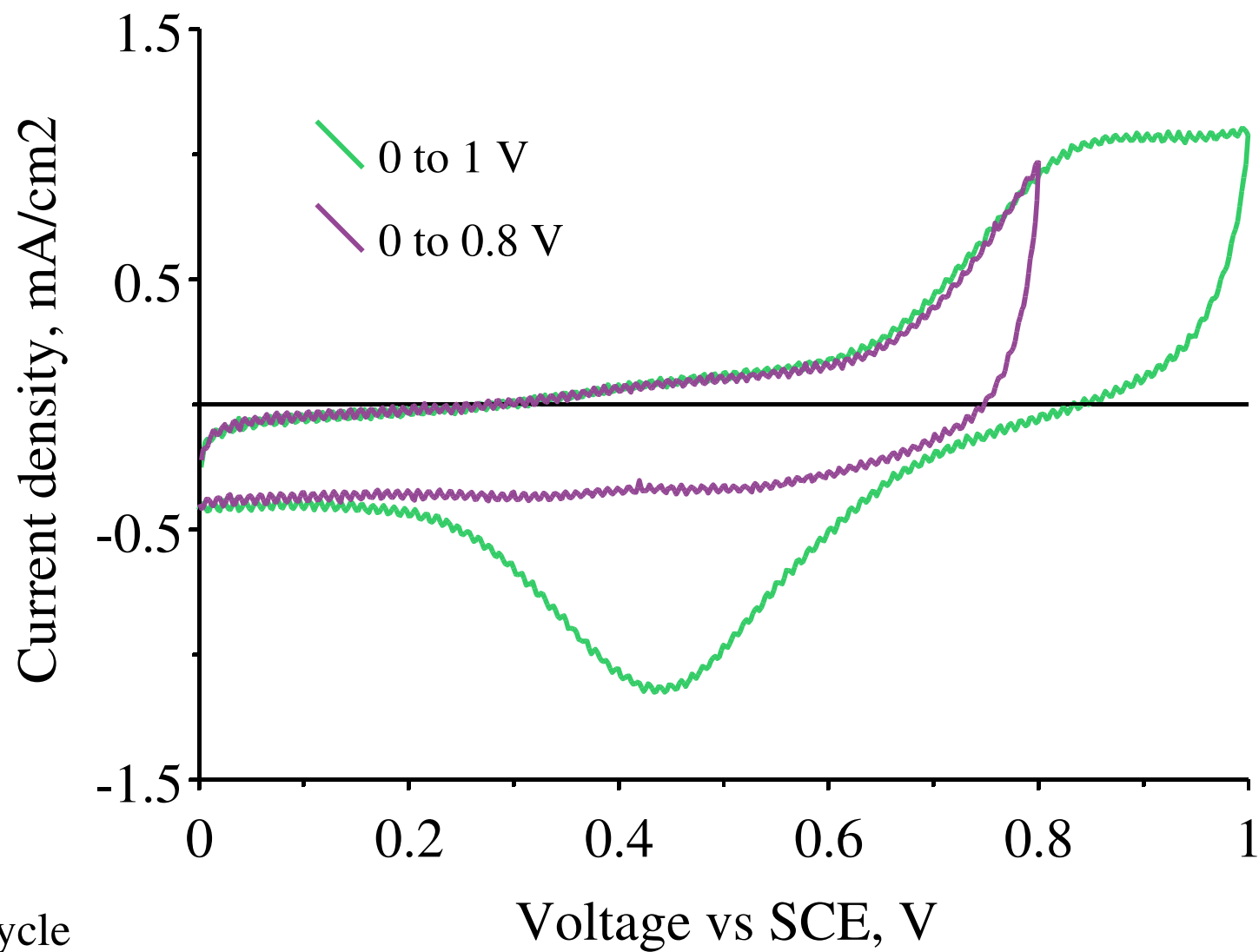Figure 5: Concentration Effects on MeOH Oxidation Peaks

10th cycle

Pt wire electrode

25 mV/s scanrate

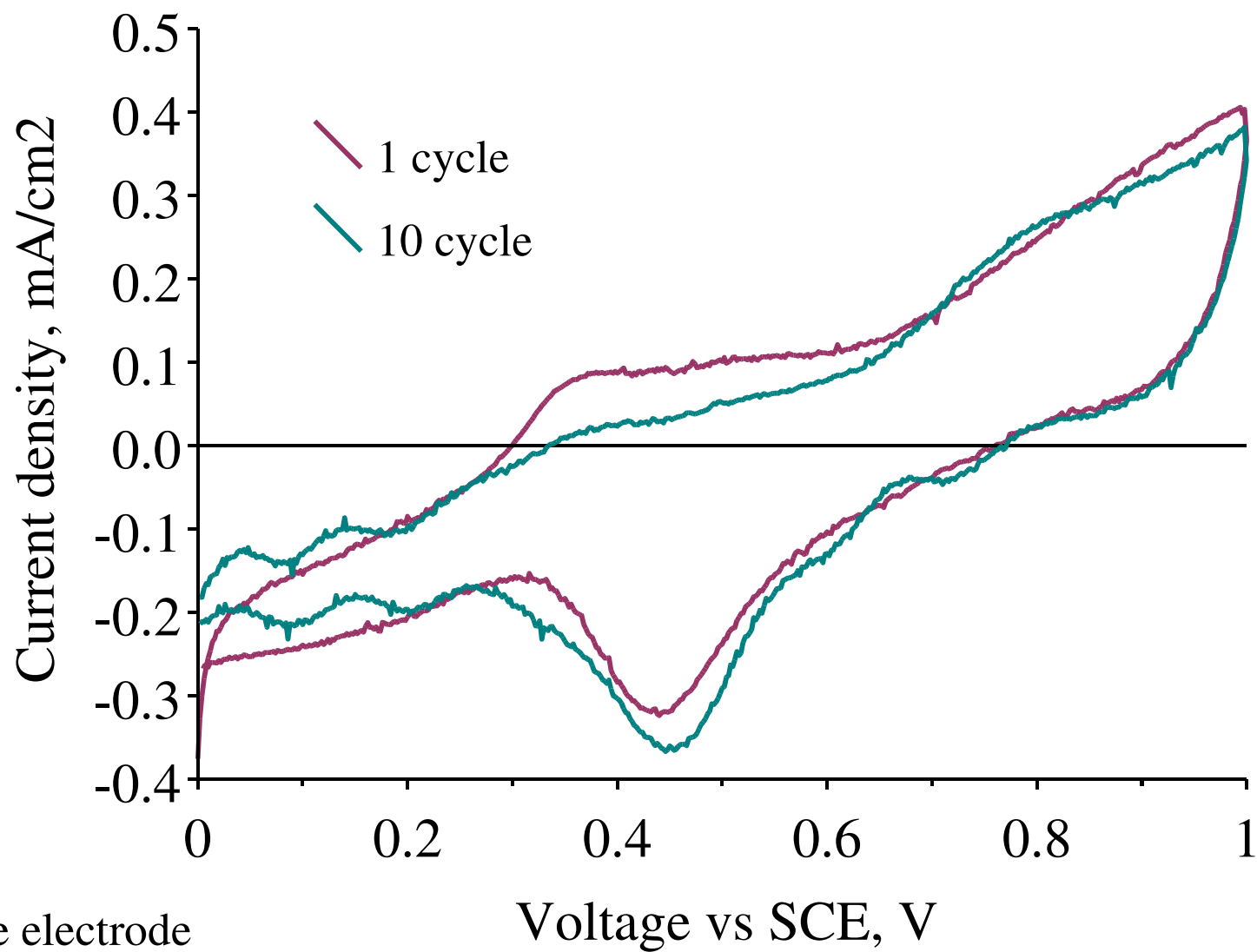Figure 6: Suppression of H2SO4 Oxidation / Reduction Peaks

10th cycle

25 mV/s scanrate

5 mM H2SO4 + 5 mM MeOH
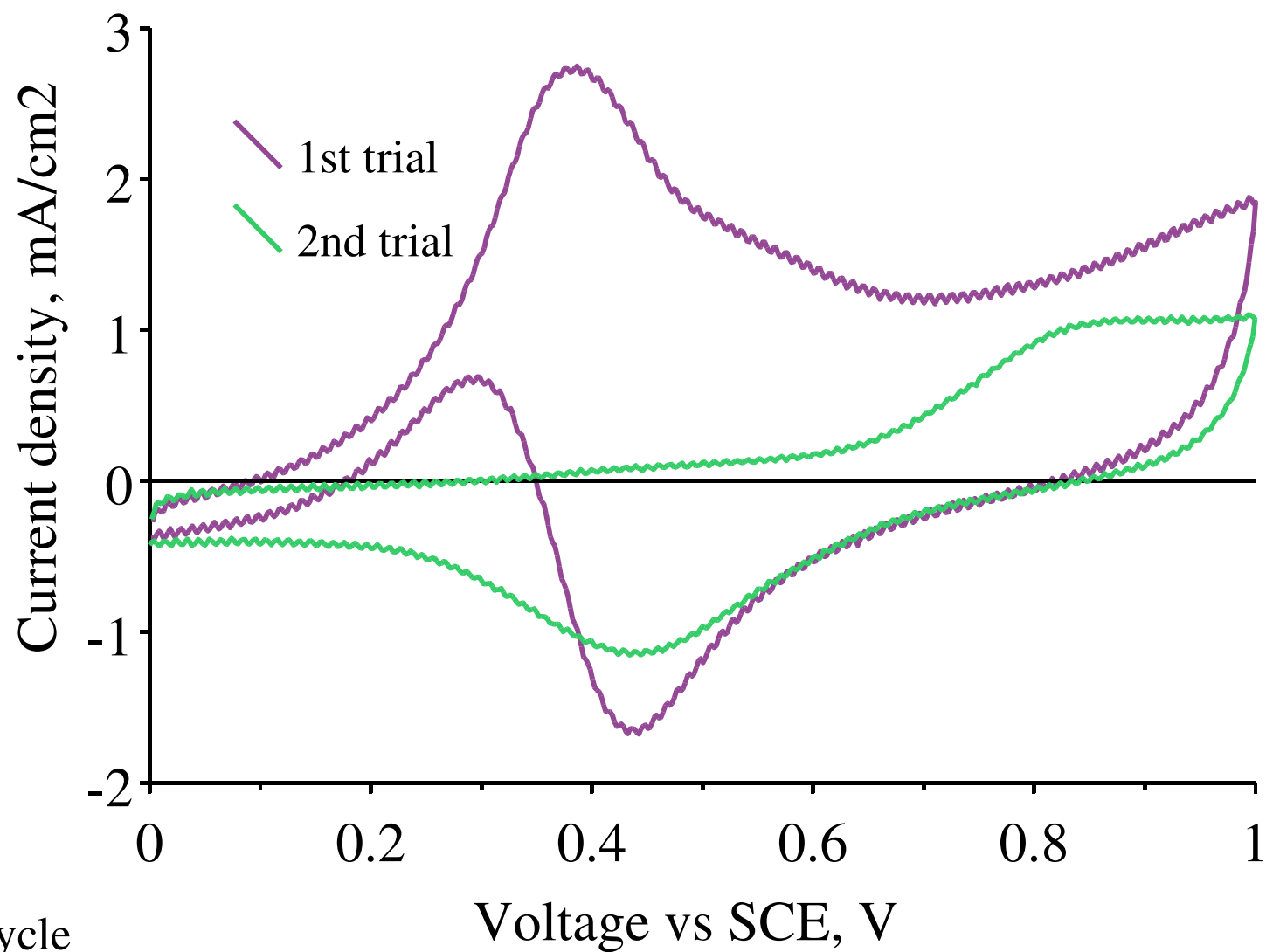
Figure 7: Another Pass at Scanrate Optimization

Pt wire electrode

5 mV/s scanrate

5 mM H2SO4 + 5 mM MeOH

Figure 8: Catalytic Activation of Pt Electrode

1st trial
2nd trial

Current density, mA/cm2

Voltage vs SCE, V

10th cycle

25 mV/s scanrate

5 mM H2SO4 + 5 mM MeOH