CHEMELECTROCHEM

Supporting Information

Electrogenerated Chemiluminescence Reporting on Closed Bipolar Microelectrodes and the Influence of Electrode Size

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Section 1: Limiting Poles in Closed Bipolar Electrochemistry

Discussion:

One of the poles will always limit the current through a closed BPE, unless both poles are equally "balanced." Considered individually, under steady-state conditions each pole will have a maximum current at a given potential. That maximum current can easily be measured by taking a CV of the individual pole in a two-electrode setup. When the two poles are connected to form a closed BPE, the current through the BPE at each potential will be limited by the individual pole with the lowest maximum current at that potential. This pole is termed the limiting pole. Figure S1 demonstrates this concept. The CV represented by the dashed black line is the two-electrode CV for a 127 µm electrode in 5 mM $Fe(CN)_6^{3-}$. The CVs represented by the dashed red and dashed blue lines are the two-electrode CVs for either a 25 µm or 50 µm electrode, respectively, in ECL solution. As seen, all three CVs exhibit steady-state behavior, with the mass transfer-limited steady-state current representing the maximum current for each electrode under the conditions present.

The solid lines show the CVs obtained when these two poles are connected to form a closed BPE. The cathode of the BPE is a 127 µm electrode and is placed in 5 mM $Fe(CN)_6^{3-}$. The anode of the BPE is either a 25 µm (red) or 50 µm (blue) electrode and is placed in ECL solution. For the BPE with the 25 µm anode, note that the magnitude of the steady-state current is equivalent to the magnitude of the steady-state current of the 25 µm electrode in ECL solution in a two-electrode setup (dashed red trace). This is because a 25 µm electrode in ECL solution has a lower magnitude steady-state current than a 127 µm electrode in 5 mM $Fe(CN)_6^{3-}$ and therefore limits the current through the BPE. Hence, in this setup, the anode is the limiting pole. Conversely, for the BPE with the 50 µm anode, the magnitude of the steady-state current is equivalent to the magnitude of the steady-state current of the 127 µm electrode in 5 mM $Fe(CN)_6^{3-}$ in a two-electrode setup (dashed black trace). This is because a 50 µm electrode in ECL solution has a higher magnitude steady-state current than a 127 µm electrode in 5 mM $Fe(CN)_6^{3-}$ and therefore does not limit the current through the BPE. Hence, in this setup, the cathode is the limiting pole.

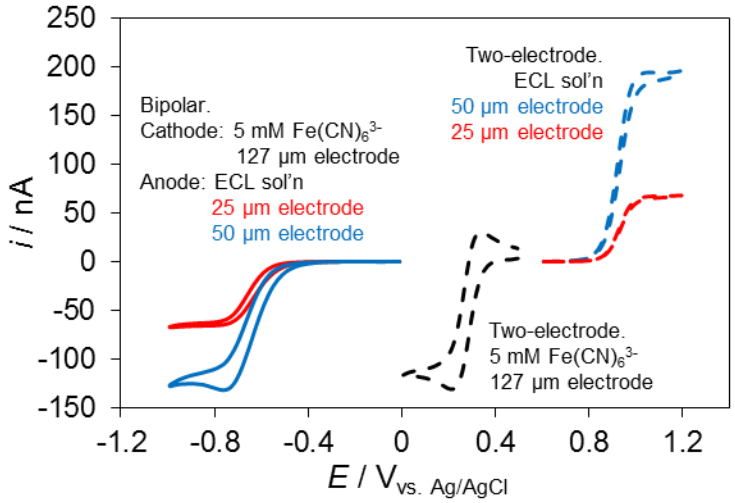

Figure S1. Relationships between two-electrode and bipolar setup currents and potentials for different size anodic poles for the detection of 5 mM $Fe(CN)_6^{3-}$. The cathodic pole in the bipolar setup was 127 µm. Dashed lines show two-electrode setup CVs, while solid lines show bipolar setup CVs.

Section 2: Data and Images from BPE Sensing Experiment

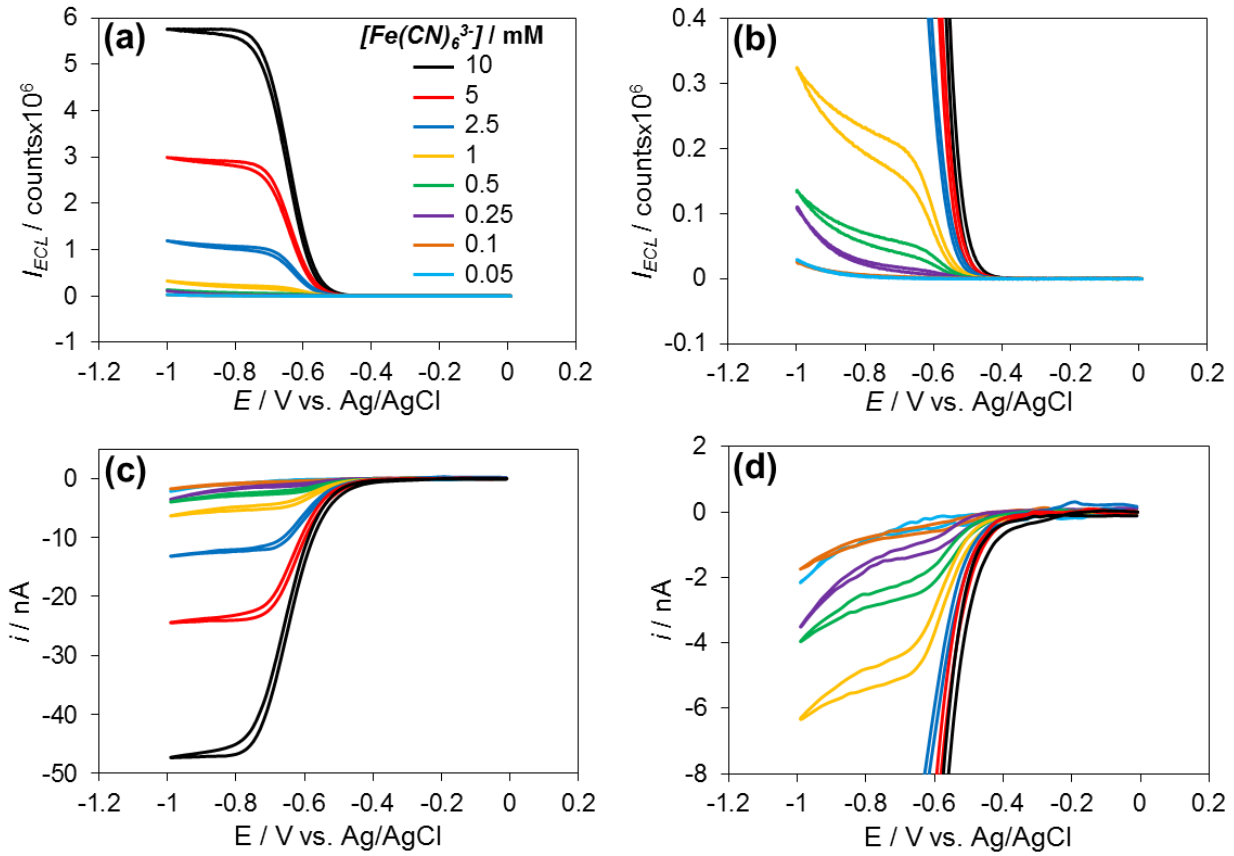

Figure S2. Traces of the simultaneously-recorded ECL intensity [(a) and (b)] and current [(c) and (d)] during the potential sweep BPE sensing experiment discussed in Figure 3 of the main text. In this experiment, the cathode was 25 µm and placed in different concentrations of $Fe(CN)_6^{3-}$, and the anode was of various sizes and placed in ECL solution. The data shown in this figure is for a 25 µm anode. (b) and (d) are zoom-ins of (a) and (c), respectively. A calibration curve is formed from this data by taking the intensity of the signal (either ECL intensity or current) at -0.8 V during the forward sweep for each concentration of $Fe(CN)_6^{3-}$. This intensity is approximated as the steady-state signal intensity, which can then be plotted against $Fe(CN)_6^{3-}$ concentration. The calibration curves from the data shown here are represented by the red circles (for ECL) and red triangles (for current) in Figure 3a of the main text.

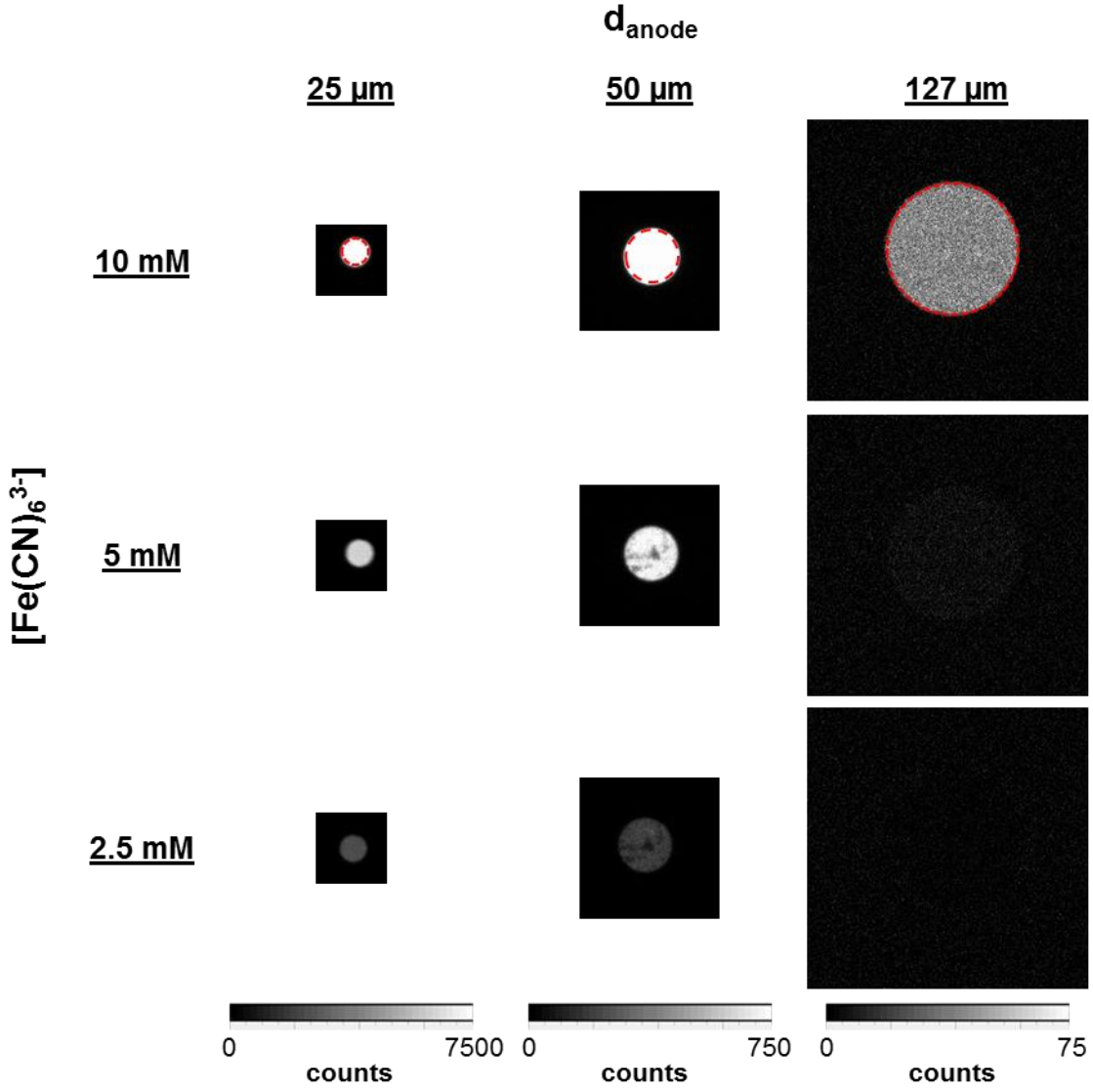

Figure S3. Images of the anodic poles of the BPEs for different cathodic concentrations of $Fe(CN)_6^{3-}$ during the BPE sensing experiment described in Figure 3a of the main text. Each image was taken at -0.8 V during the forward sweep of the potential scan. The integrated counts over each anode gives the total ECL intensity, which are the steady-state ECL intensity values reported in Figure 3a of the main text. The cathodic pole in all cases was a 25 µm electrode. Note the different intensity scales for the images of each anode size. The actual anode positions are indicated by the dashed red rings.

Section 3: Enhanced Signal to Noise Ratio on Smaller Anodes

Discussion:

As mentioned in the main text, if an equivalent ECL intensity is found on two electrodes of different sizes, the signal to noise ratio will be greater on the electrode of smaller size if a pixel-based detector (such as a CCD camera, which is used here) is used. While a pixel-based detector is not necessary in a one-electrode sensing experiment, it becomes necessary if one desires to do sensing/imaging on an electrode array due to the need to image several electrodes simultaneously. This signal to noise effect can be thought of in two ways. If considering the total ECL intensity (i.e. integrating the intensity over the entire electrode area), a larger electrode will give a larger noise value. This can be seen, somewhat subtly, in the ECL intensity traces displayed in Figure S4a below, and can be very clearly

seen in Figures 3b and 4b of the main text. This is because a larger electrode requires a larger area (and hence a larger number of pixels) to be integrated to get the total ECL intensity. As long as the same camera settings are used, the per pixel noise level remains constant regardless of electrode size. This means the increased noise associated with the total ECL intensity of a large electrode is due to multiplying the per pixel noise by a larger factor due to using more pixels to measure the ECL signal. If considering the per pixel ECL intensity (i.e. an image), a larger electrode will have a smaller signal per unit area, corresponding to a smaller signal per pixel on the camera. This is because the same total ECL signal is emitted from a larger area, meaning a large electrode effectively "spreads out" the signal. This causes a lower per pixel signal to noise ratio, and can be clearly seen in the images in Figure S4b below.

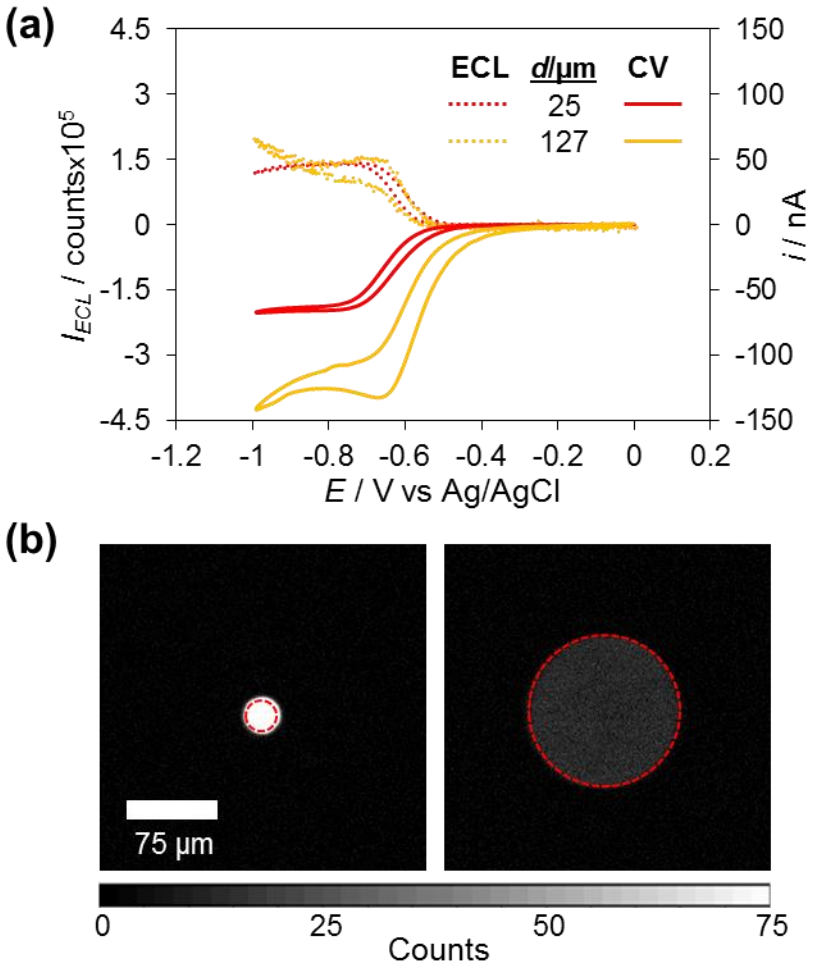

Figure S4. Results of a BPE sensing experiment in which the cathode was 127 µm and placed in 5 mM $Fe(CN)_6^{3-}$. The anode was either 25 or 127 µm and placed in ECL solution. (a) The total ECL intensity (dashed lines) and current (solid lines) for each anode size during a potential sweep from 0 to -1 V. As seen, the steady-state ECL intensities are approximately the same for both anode sizes. Discussion of why this is (and relatedly, why the current magnitudes are different) can be found in the main text. (b) Images of each anode at -0.8 V during the forward sweep of the potential scan. Despite having approximately the same total ECL intensities, one can clearly see that the signal to noise ratio of the 25 µm anode is markedly better than that of the 127 µm anode. The actual anode positions are indicated by the dashed red rings.

Section 4: Electrochemical Oxidation of TPrA on Anode

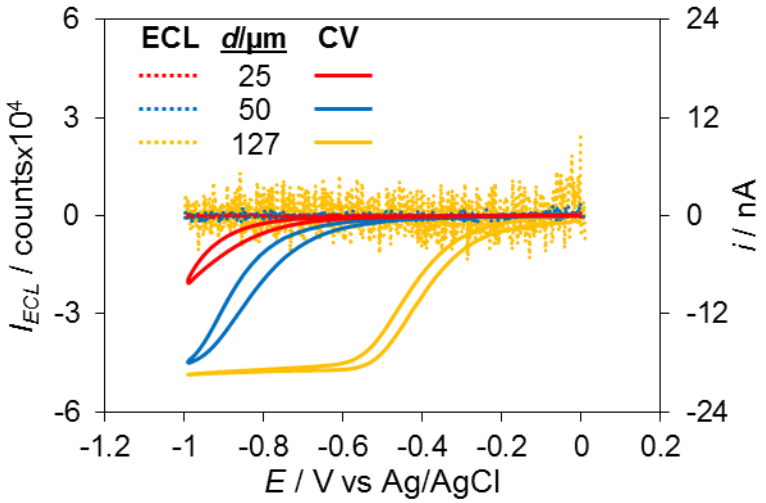

Figure S5. Results of a bipolar coupling experiment in which the reporting pole was immersed in a solution of 25 mM TPrA and 0.1 M pH 7.0 phosphate buffer (no Ru(bpy)32+). The analyte pole was a 25 µm Pt electrode and immersed in a solution of 5 mM ferricyanide with 1 M KCl. The reporting pole was either a 25, 50, or 127 µm Pt electrode. A potential sweep from 0 to -1 V at 20 mV/s was applied to two Ag/AgCl driving electrodes and the current through the BPE and light emission from the reporting pole were simultaneously recorded. This experiment is the same as that shown in Figure 3b of the main text, except Ru(bpy)32+ is not present in the reporting pole solution used here. As can be seen, no light emission is observed from the reporting poles. This is expected as the ECL process cannot occur without Ru(bpy)32+ oxidation. The CV traces clearly show that increasing the size of the reporting pole increases the amount of current that passes through the BPE at a given potential, with larger currents passing at potentials closer to 0 V as the reporting pole size increases. For the 127 µm reporting pole, the steady-state current (limited by the analyte pole) is reached before -0.6 V (the approximate onset potential of ECL emission as determined in Figure 3b). As no Ru(bpy)32+ was used in the experiment here, this shows that the steady-state current can be reached with solely TPrA oxidation occurring on the reporting pole. This explains why no ECL emission is observed for the 127 µm electrode in Figure 3b. For the 50 and 25 µm reporting poles, TPrA oxidation is only able to support a fraction of the steady-state current, meaning that in a typical ECL solution (i.e. one containing Ru(bpy)32+), Ru(bpy)32+ oxidation will still occur and there will be ECL emission from the electrode.

Section 5: Comparison of Experimental and Predicted Calibration Curves

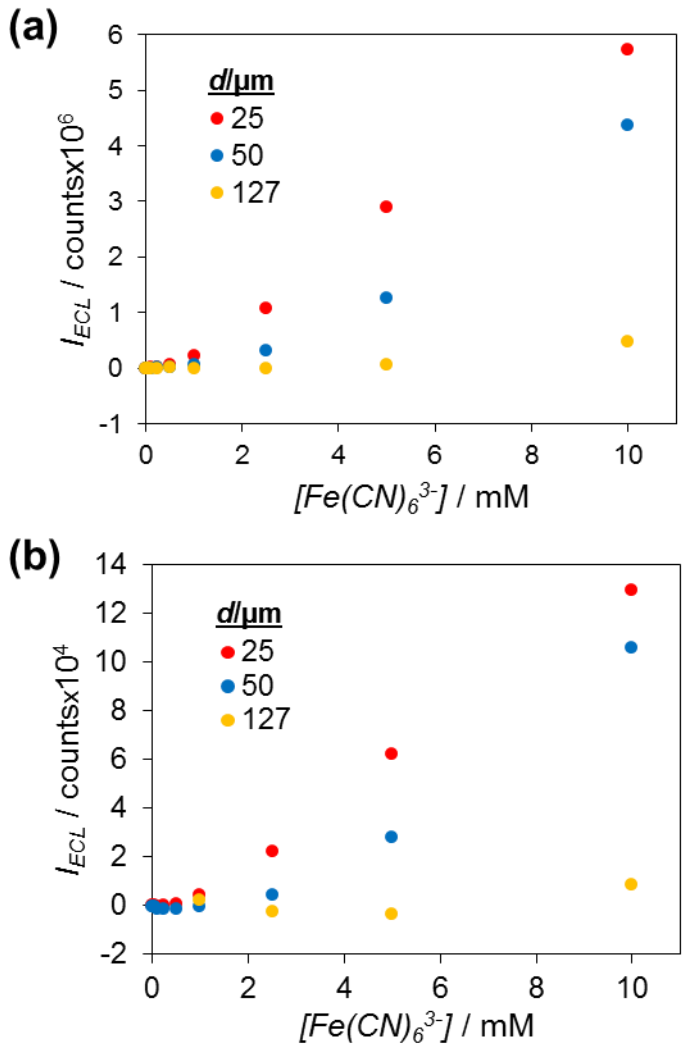

Figure S6. Side-by-side comparison of the experimental (a) and predicted (b) calibration plots for the BPE detection of $Fe(CN)_6^{3-}$ using a 25 µm cathode and various sized anodes. Both of these plots are displayed separately in the main text. The data in (a) is shown in Figure 3a, and (b) is shown as Figure 5. The differences in ECL intensity magnitude between the plots are because an EM gain of 50 was used to acquire the data in (a), while no EM gain was used to acquire the data used to make the predicted curves shown in (b). Therefore, the intensities in (a) are ~50 times greater than the intensities in (b).

Section 6: ECL Signal vs. Current in Two-Electrode Setup for Different Electrode Sizes

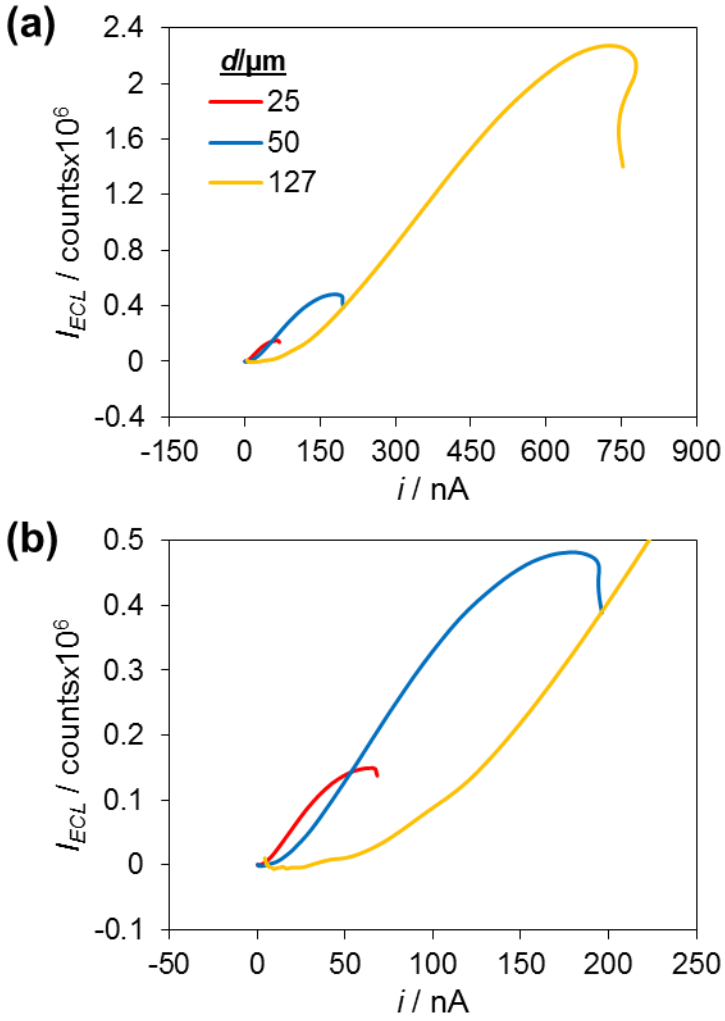

Figure S7. Plots of ECL intensity vs. current for the three different electrode sizes in a two-electrode setup. (b) is a zoom-in of (a). These plots are made from the same data shown in Figure 4 of the main text. In this experiment, a Pt electrode serves as the working electrode and is placed in the ECL solution. A potential sweep from 0.6 to 1.2 V at 20 mV/s is applied while simultaneously monitoring the ECL intensity and the current. Only the forward scan is shown in these plots. These plots clearly demonstrate a couple of key points. First, the ECL intensity is higher at lower currents for smaller electrodes. Second, the ECL intensity levels off to a steady-state maximum for each electrode. As the electrode size increases, this maximum increases in magnitude and is reached at higher currents. The behavior of the ECL signal in BPE sensing experiments can be readily explained from plots like these. With knowledge of the current that an analyte will produce at the cathode, the ECL intensity from each anode can be easily predicted using this plot by taking the ECL intensity at that current for each anode.

Section 7: Predicting Calibration Curves for BPE Sensing Using 127 µm Cathode

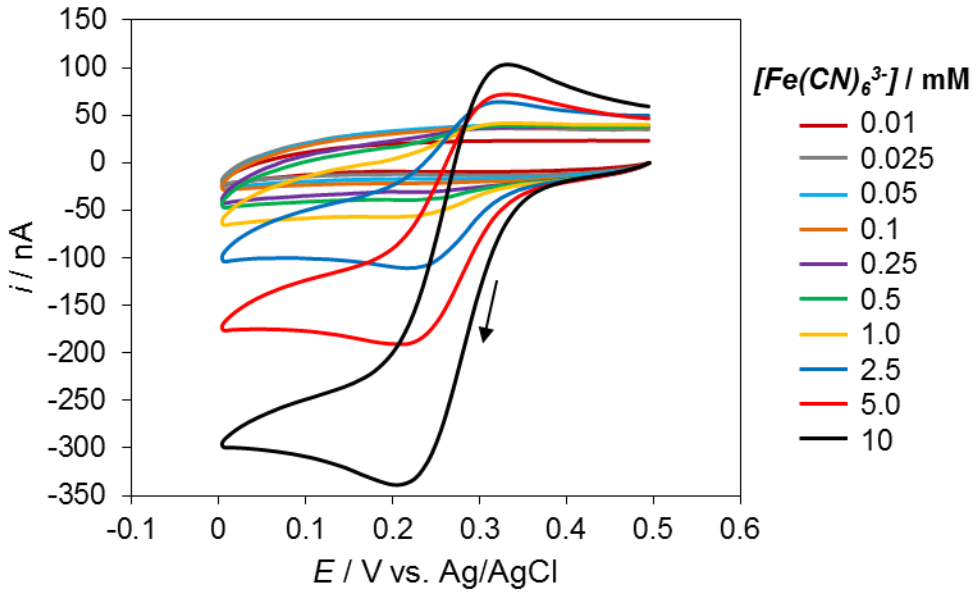

Figure S8. CVs obtained for different concentration of ferricyanide in 1 M KCl using a 127 µm Pt electrode in a two-electrode setup. The potential was swept from 0.5 to 0 V at 20 mV/s. The forward scan is indicated by the black arrow. The steady-state current for each concentration was approximated as the current at 0.1 V during the forward sweep.

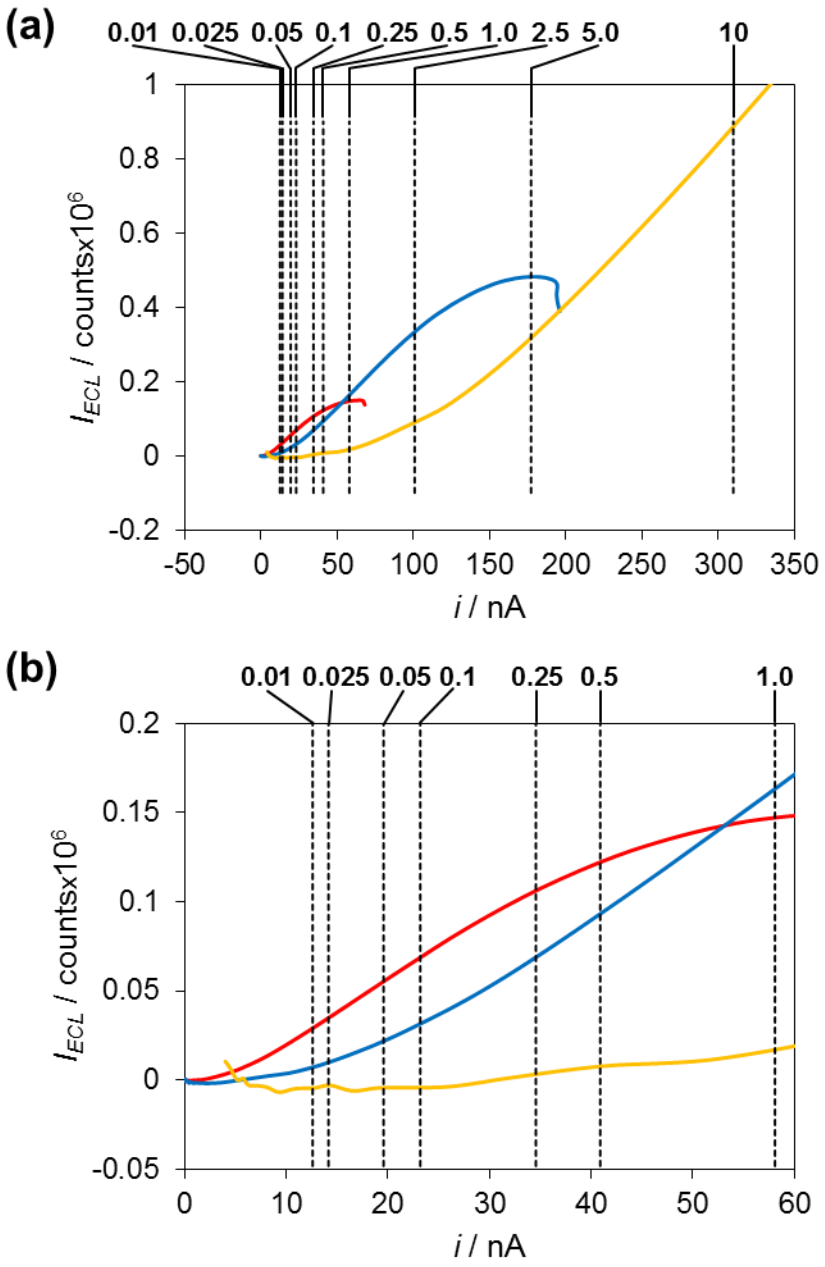

Figure S9. Plots of two-electrode ECL intensity vs. current for each electrode size overlaid with the steady-state currents measured for each ferricyanide concentration using a 127 µm Pt electrode. The ECL intensity vs. current plots are the same as those presented in Figure S7. The vertical dashed black lines represent the steady-state current measured for a particular ferricyanide concentration using a 127 µm Pt electrode. The steady-state currents were taken as the current at 0.1 V in the forward sweep of the CV data presented in Figure S8. The numbers above the dashed black lines indicate ferricyanide concentration in mM. As in Figure S7, (b) is a zoom-in of (a) and the red, blue, and yellow traces are for a 25, 50, and 127 µm electrode, respectively. A calibration plot for the BPE sensing of ferricyanide using a 127 µm cathode and a given size anode can be predicted from this data by taking the ECL intensity for a given electrode size at each steady-state current marked and plotting those intensities against the respective $Fe(CN)_6^{3-}$ concentration. For example, the predicted calibration curve for a 127 µm anode (shown by the yellow points in Figure 6a of the main text) is given by plotting the ECL intensity at each point where the ECL curve (solid yellow line) is intersected by a vertical dashed black line against the respective ferricyanide concentration represented by each steady-state current.