Supporting Information

Alternating Current Voltammetry at a Bipolar Electrode with Smartphone Luminescence Imaging for Point-of-Need Sensing

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Evaluation of ECL intensity following a DC potential step.

The luminescence response generated from an applied potential (1.0 V – 1.5 V) is compared with the simultaneously obtained current density. The luminescence is collected with both a microscope equipped with a sCMOS camera and a smartphone camera. The current density and luminescence intensity values were obtained by averaging values over a period of 0.5 s, $t = 1.0$ s after the potential was applied.

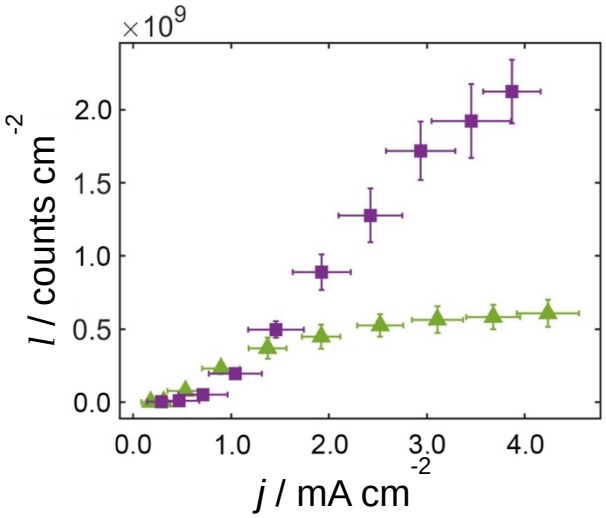

Figure S1. Luminescence efficiency for the ECL reaction with two types of detectors, a microscope camera (purple squares) and a smartphone camera (green triangles). The current density (j) obtained from a 3-electrode configuration is plotted against the luminescence intensity (l) obtained.

Luminescence generated during ACV imaged at faster frame rates.

Although the J_p of the ECL mixture was observed to increase with increasing frequency (main text), it was found that L_p, obtained in the same experiment, decreased with increasing frequency. To determine if this phenomenon was caused by undersampling, in which case the frequency is too fast to measure the amplitude accurately with the given frame rate, the light micrscopy was used to detect the luminescence response from the ECL mixture, under ACV interrogation, at several frame rates. Two frame rates were tested along with the 20 fps frame rate: 50 fps and 100 fps. **Figure S2a** shows luminescence voltammograms obtained at 1.0 Hz for each of these frame rates. The intensities are normalized by exposure time to put them on the same scale as the result obtained at 20 fps. The variation in L_p appears to be random and falls within that expected for replicates. Therefore, we conclude that the frame rate does not significantly impact L_p obtained for ACV at 1.0 Hz. However, it appears that for the 5.0 Hz perturbation, 20 fps does not capture the full oscillation in the luminescence, because L_p is about 38% lower than that obtained at the faster frame rates (**Figure S2b**). Despite this loss of signal, we find that 20 fps can still be utilized to obtain quantitative information from the 5.0 Hz ACV because the relative magnitude of L_p (versus a calibration curve obtained at 5.0 Hz) and the peak location (E_p) are unaffected. A critical point is that even at the faster frame rates, L_p at 5.0 Hz remains lower than L_p at 1.0 Hz, despite the increase in J_p. Further investigation is required to explain this phenomenon.

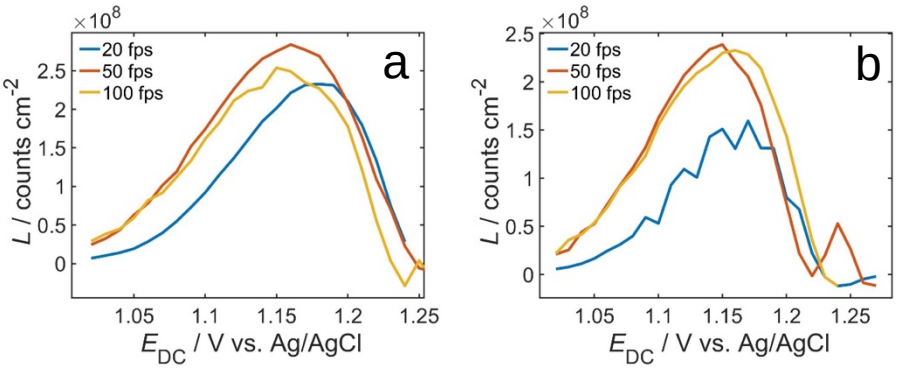

Figure S2. Amplitude of the luminescence response of the ECL mixture imaged with the microscope camera at three different frame rates, 20 fps (blue), 50 fps (red), and 100 fps (yellow), during ACV obtained at two different frequencies a) 1.0 Hz and b) 5.0 Hz. The data is normalized by exposure time.

Evaluation of ECL intensity during ACV with microscope camera detection.

Following an approach similar to that utilized to obtain the data of **Figure 1** in the main text, raw luminescence responses were obtained by light microscopy for the ECL reaction responding to an ACV at 1.0 Hz (**Figure S3a**) and 5.0 Hz (**Figure S3c**) on a traditional 3-electrode configuration. In both cases, images were captured at a rate of 20 fps. Additionally, the peak amplitude response to both current density and luminescence intensity is plotted for the two frequencies (**Figure S3b,d**). Peak shape and position and relative intensities are in agreement with the data of **Figure 1**, which was obtained with a smartphone as the detector.

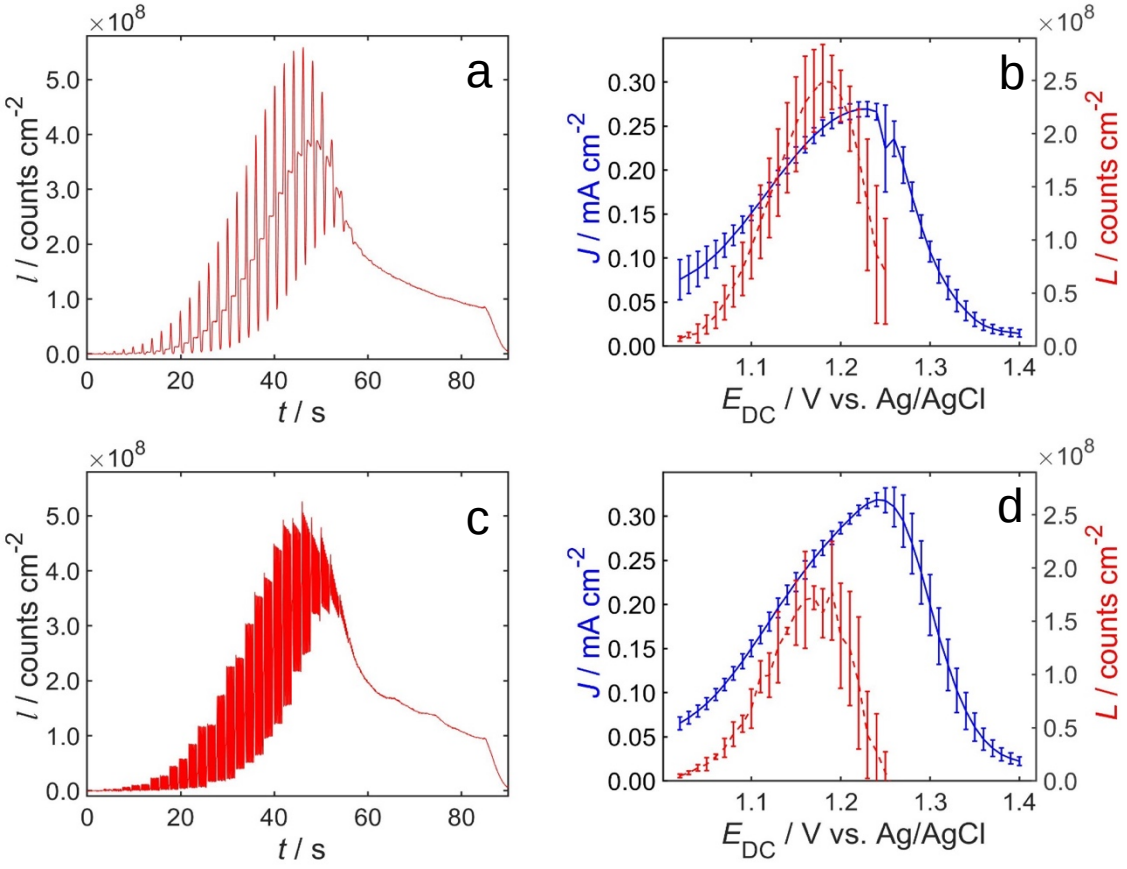

Figure S3. Response of ECL reaction solution to ACV on a 3-electrode cell configuration. Luminescence data is obtained with a microscope camera (20 fps). Raw luminescence (I) response obtained over time to ACV at a) 1.0 Hz and c) 5.0 Hz. Average amplitude of the current density (J, blue line) obtained from 3 devices, with corresponding average amplitude of luminescence (L, red line) for b) 1.0 Hz ACV and d) 5.0 Hz, plotted against the applied DC step potential.

DC and AC current response comparison for sensing and reporting reactions.

As demonstrated in **Figure 4** of the manuscript, a linear response between both peak amplitude of the luminescence intensity (L_p) and peak amplitude of the current density (J_p) with concentration is maintained at low ferricyanide concentrations. This trend appears because the sensing reaction is limiting the amount of current that flows through the BPE. At high concentrations of ferricyanide, the response of the luminescence and current are no longer

impacted by the increased ability of the sensing reaction to supply current. In this regime, the reporting reaction limits the current flowing through the BPE, despite the fact that the effective concentration of the reporting solution is higher than that of the sensing solution. The results of **Figure S4** provide an explanation for this observed behavior. The DC (dashed lines) and AC (solid lines) components of the current density obtained for the reduction of ferricyanide and the ECL reaction are plotted in **Figure S4a** and **b**, respectively. While the peak DC current density is higher for ECL than for ferricyanide, the J_p is lower due to insufficient reversibility of this reaction. In other words, the ECL reaction is too slow kinetically to follow the alternating potential that is being applied.

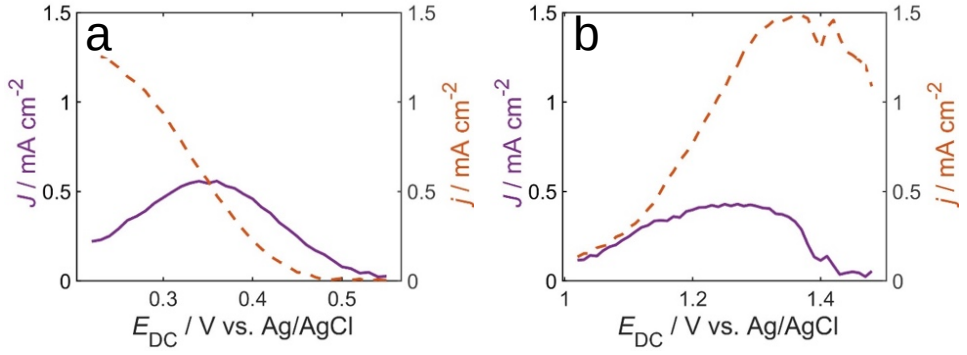

Figure S4. Components of the AC voltammetric response for a) ferricyanide and b) $Ru(bpy)_3^{2+}$ with co-reactant TPA on a 3-electrode cell. The DC current density (j, orange dashed line) and the amplitude of the AC current density (J, purple solid line) are plotted against the DC potential step applied (E_{DC}) for each case.

Characteristics of AC voltammograms obtained at a BPE that couples ferricyanide reduction to the ECL reaction.

Here, we investigate the features of AC voltammograms obtained at a BPE for ferricyanide reduction coupled to the ECL reaction. Under the condition that a low concentration of ferricyanide is present at the BPE cathode, a single peak in the amplitude of the current density (J) occurs in the AC voltammogram near $\Delta E_{tot} = 0.6$ V, as in **Figure S5a**. As the concentration of ferricyanide is increased, the peak height increases and it gradually shifts to $\Delta E_{tot} = 0.85$ V. At 4.0 mM ferricyanide, a second peak is observed at about $\Delta E_{tot} = 1.0$ V (green line, **Figure S5a**). We attribute the appearance of this second peak to an increased ability of the BPE cathode to supply current beyond the capacity of the ECL reaction (BPE anode). As a result, E_{BPE} shifts more positive to access a different set of reactions (e.g., ferricyanide reduction coupled to water oxidation). The $L_p$occurs slightly after the first peak (**Figure S5b**). This observed behavior indicates that the luminescence ACV corresponds to the desired pair of redox reactions (reduction of ferricyanide and oxidation of the ECL mixture). Interestingly, the luminescent AC voltammogram becomes narrower as the concentration of the ferricyanide increases (**Figure S5c**). We hypothesize that this trend may occur because the ferricyanide reduction reaction was coupled to a steeper segment of the ECL i-E curve.

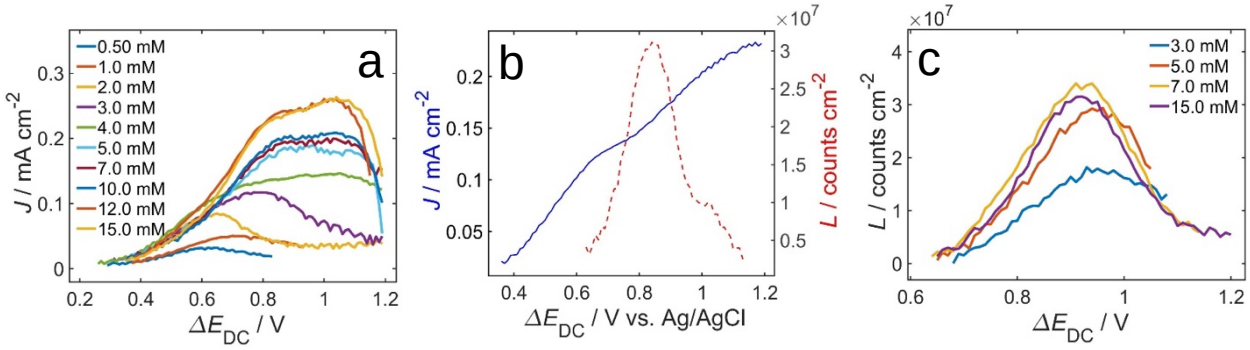

Figure S5. a) Amplitude of the alternating current density (J) for several distinct concentrations of ferricyanide (0.5 mM – 15.0 mM) at the BPE cathode. b) Amplitude of the alternating current density (J, blue solid line) and amplitude of the luminescence (L, red dashed line) for a BPE configuration with 10.0 mM ferricyanide at the BPE cathode, and the ECL mixture on the reporting end of the BPE (anode). c) Amplitude of the alternating luminescence (L) for several distinct concentrations of ferricyanide at the BPE cathode.