Supporting Information for

Mapping the Distribution of Potential Gradient in Bipolar Electrochemical Systems through Luminol Electrochemiluminescence Imaging

Elena Villani,[†] and Shinsuke Inagi*,[†,‡]

[†]Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan
[‡]PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

*Corresponding author: inagi@cap.mac.titech.ac.jp

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Electrochemistry and ECL of luminol/H₂O₂ system used in this study

(a)

Luminol 10 mM + H₂O₂ 30 mM in NaOH 0.1 M
Luminol 10 mM in NaOH 0.1 M
H₂O₂ 30 mM in NaOH 0.1 M
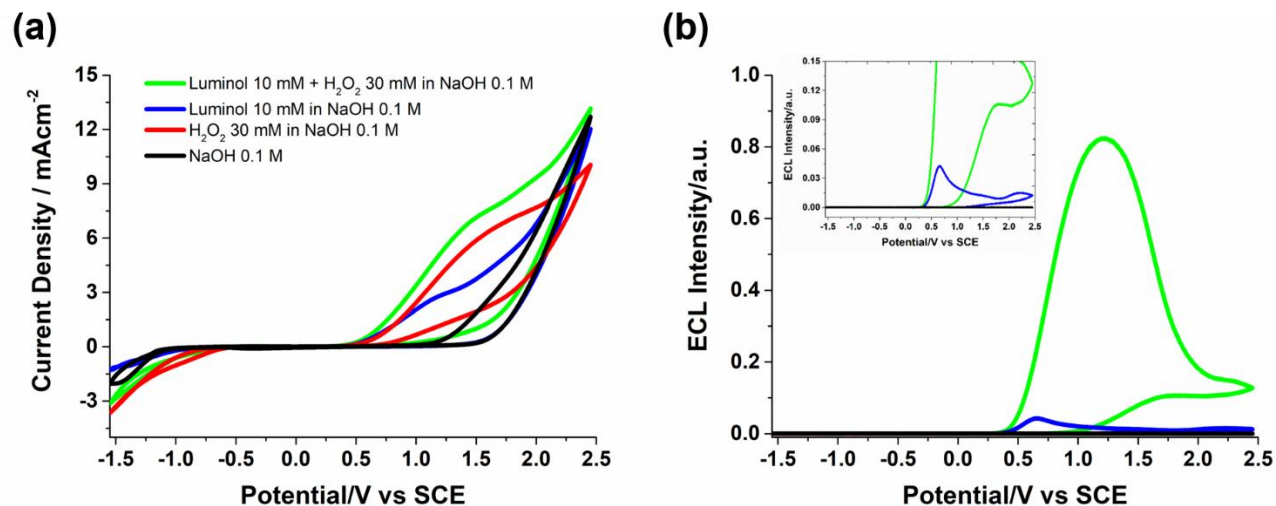NaOH 0.1 M

(b)

Figure S1. (a) Cyclic voltammetry and (b) correspondent ECL emission of the single chemical species that constitute the solution used in this study on an ITO electrode. Inset in figure (b): magnification of ECL emission. Scan rate: 100 mV/s. PMT bias: 250 V.
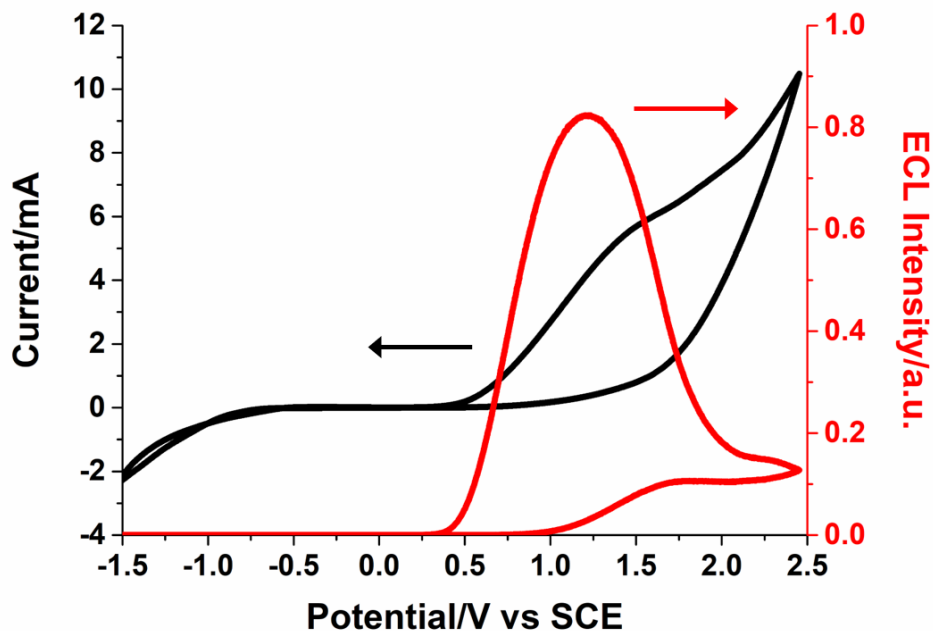

Figure S2. Cyclic voltammetry (black line) and correspondent ECL emission (red line) for a solution containing luminol 10 mM and H₂O₂ 30 mM in NaOH 0.1 M, pH 12.6, on an ITO electrode. Scan rate: 100 mV/s. PMT bias: 250 V.
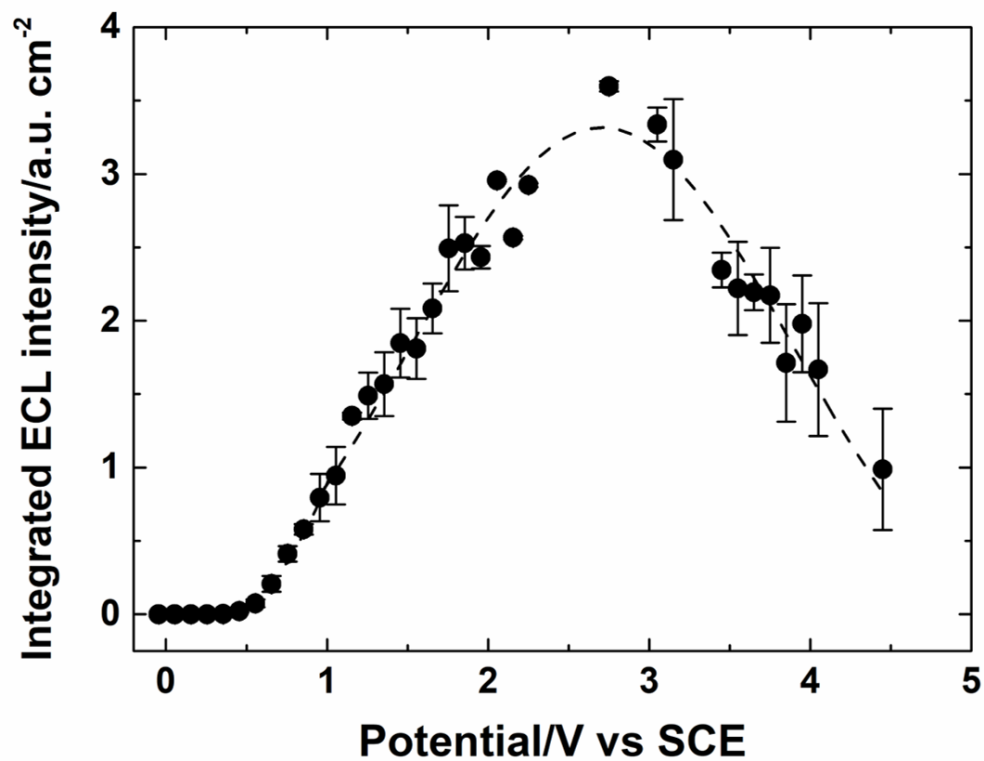
Figure S3. Integrated ECL intensity as a function of the potential applied on an ITO electrode. Integrated ECL values were obtained by chronoamperometry ($E_1 = 0$ V, $t_1 = 1$ s; $E_2 =$ from 0 V to 4.5 V, $t_2 = 1$ s) in a solution containing luminol 10 mM and H_2O_2 30 mM in NaOH 0.1 M, pH 12.6. PMT bias: 250 V. Error bars show standard deviation (n = 3). Black dashed line is a guide for the eyes.

Method to estimate the potential difference on a BPE using ECL

In this section, we report how to estimate the potential difference on a BPE placed in a certain type of bipolar electrochemical configuration using ECL.

From imaging analysis of the ECL photographs, two-dimensional ECL intensity profiles are obtained by plotting a line of pixels of known distance running through the BPE apex, starting from the anodic edge of the BPE. The resulting graph is a plot of Gray Values *vs* distance (black curve in Figure S4). The calibration curve obtained in Figure S3 (ECL intensity *vs* potential, red circles) is successively superimposed on the ECL emission profile, generating a four-axis plot where the distance from the BPE anodic edge (bottom *x* axis) with a certain value of ECL intensity correlates with the potential (top *x* axis) that has the same value of ECL intensity (Figure S4).
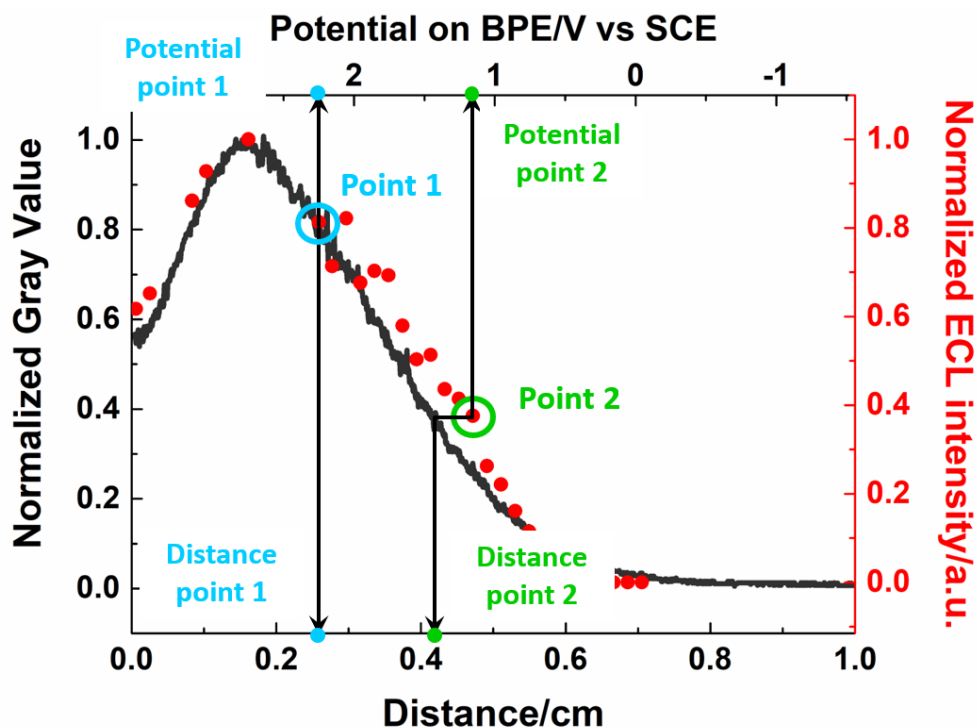

Figure S4. Four-axis plot resulting from the superimposition of two-dimensional ECL intensity profile at a certain value of E_{tot} (black curve) with the calibration curve ECL intensity *vs* potential obtained in Figure S3 (red circles).

Successively, the correspondent potential-distance data are collected from every point of the calibration curve (potential range from 0 to 4.5 V), correlating potential and distance with the same ECL intensity (e.g. points 1 and 2 in Figure S4). The final graph is a plot of potential *vs* distance and the slope obtained from the linear fitting represents the variation of the potential difference respect to the distance from the anodic edge of the BPE (Figure S5).
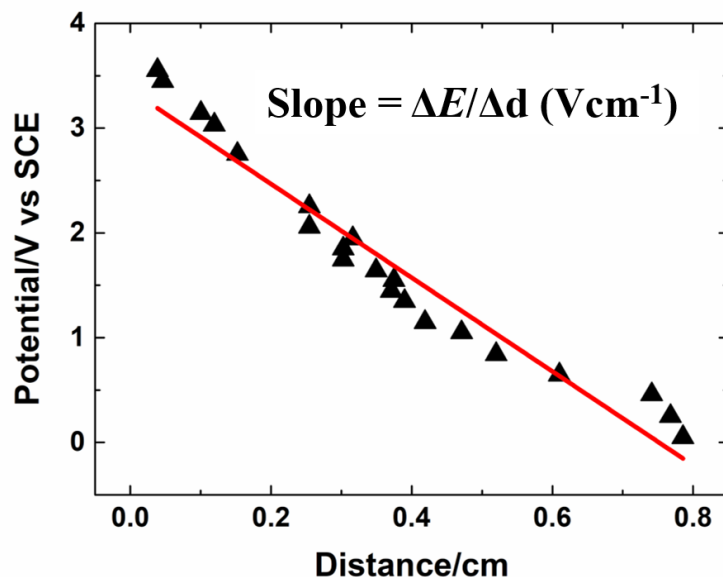
Figure S5. Plot resulting from the collection of potential-distance data obtained from Figure S4, and it corresponds to the potential difference at the BPE *vs* distance starting from the anodic edge where ECL emission is generated (black triangles). Red line represents the best linear fit.

We assume that, in our experimental conditions, the electric field generated in the electrolytic solution is not significantly affected by the faradaic processes occurring at the BPE surface and, hence, its variation is linear across the electrolyte. However, in some circumstances, the faradaic current generated at the BPE can cause a local decrease of the electric field above the electrode; in such a case, the potential drop above the BPE might deviate from linearity. This effect, called *"faradaic depolarization"*,[1-3] becomes significant when the solution above the BPE is restricted (e.g. by using microchannels with small channel heights) and the electrolyte conductivity is decreased (e.g. by lowering the concentration of the electrolytic solution). In our case, all experiments have been conducted using both bipolar configurations where there is no constriction of the solution above the BPE and electrolytic solutions with high conductivity (0.1 mol/L NaOH). In such a case, it is possible to assume that the electric field is not significantly affected by the faradaic reactions at the BPE and linearly varies across the electrolyte; hence, a linear fit can be used to evaluate the variation of the potential difference at the BPE for all bipolar configurations studied (red line in Figure S5).

Experimental set-up for ECL imaging acquisition, two-dimensional ECL intensity profiles and expected potential distribution on BPE
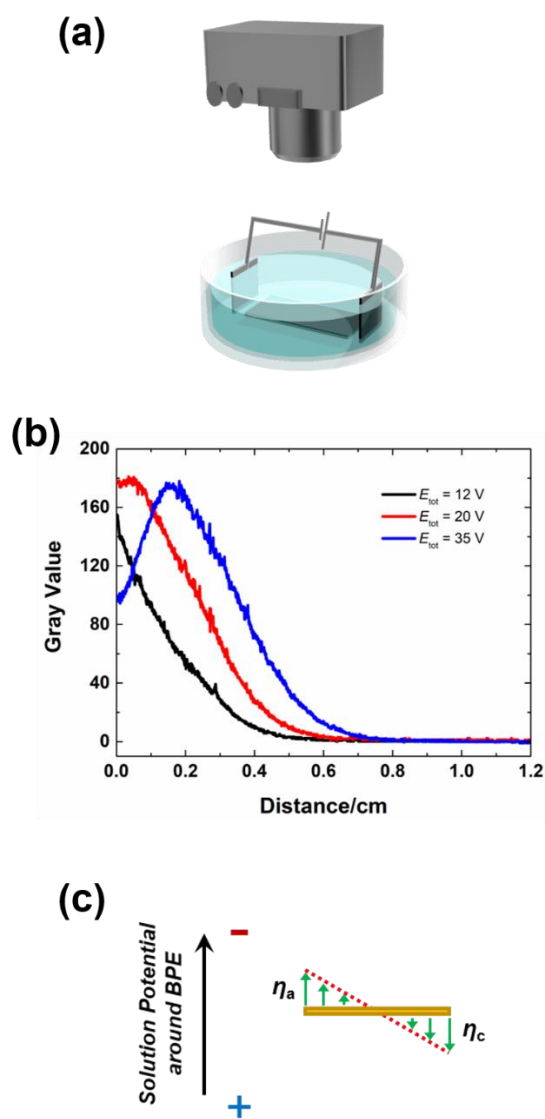
(a)

(b)

(c)

Figure S6. (a) Experimental set-up for ECL imaging studies for the linear configuration. An ITO plate (2 cm × 1 cm) was placed in between the driving electrodes and immersed in the electrolytic solution containing the ECL precursors. The camera was placed at a fixed distance on the top of the cell and the ECL emission was recorded directly from the ITO surface. (b) Two-dimensional ECL intensity profiles of the correspondent images reported in Figure 2. (c) Expected potential profile on the BPE surface for the linear configuration; η_a and η_c symbols indicate the anodic and cathodic overpotential, respectively.
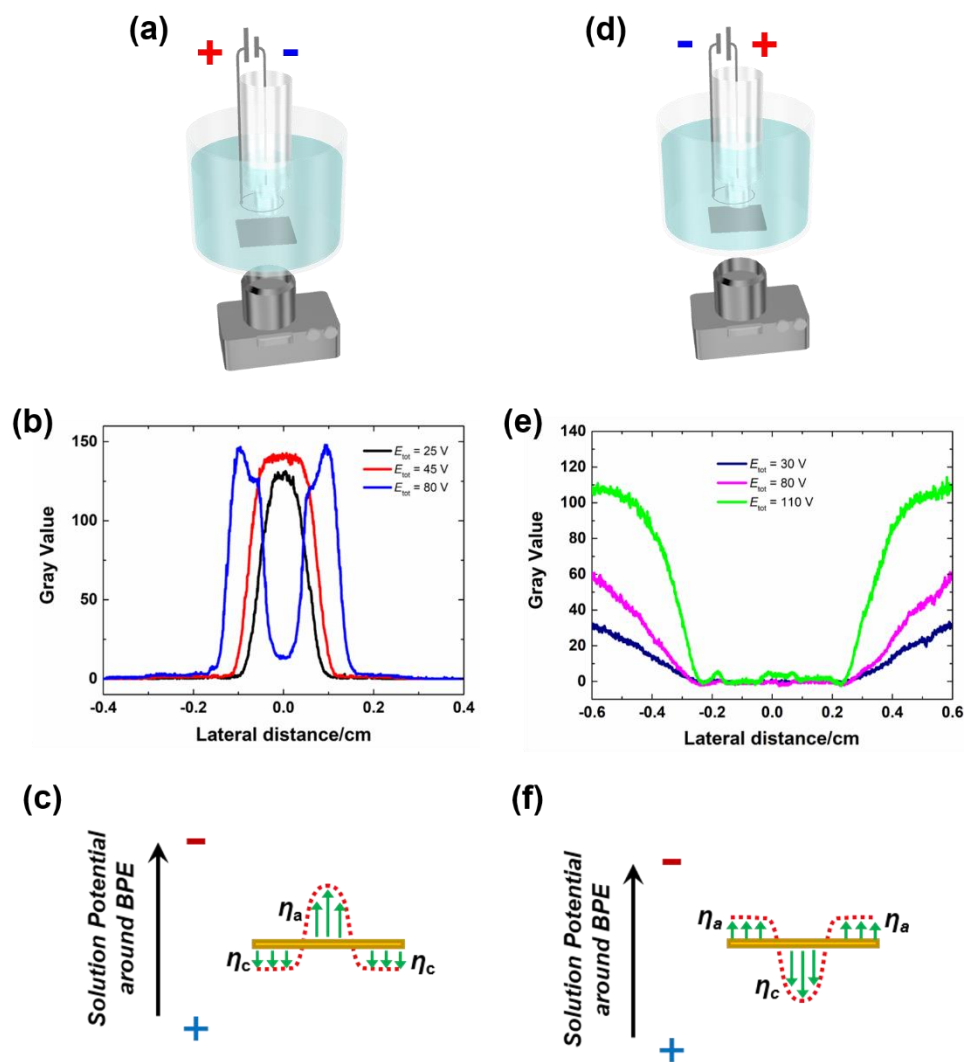
Figure S7. (a) and (d) Experimental set-up for ECL imaging studies for the cylinder configuration. The ITO plate (1 cm × 1 cm) was positioned at the bottom of the electrochemical cell with the cylinder positioned on the top of it with a distance between BPE and cylinder of 1 mm. This distance was kept constant for all studies. The camera was placed on the bottom of the electrochemical cell and the ECL emission was recorded from the back side of the ITO plate. Configuration (a) is with the anode as the outer driving electrode and the cathode as the inner driving electrode, while for configuration (d) the electrodes' disposition is reversed. (b) and (e) Two-dimensional ECL intensity profiles of the correspondent images reported in Figure 3. (c) and (f) Expected potential profiles on the BPE surfaces for the cylinder configuration; η_a and η_c symbols indicate the anodic and cathodic overpotential, respectively.
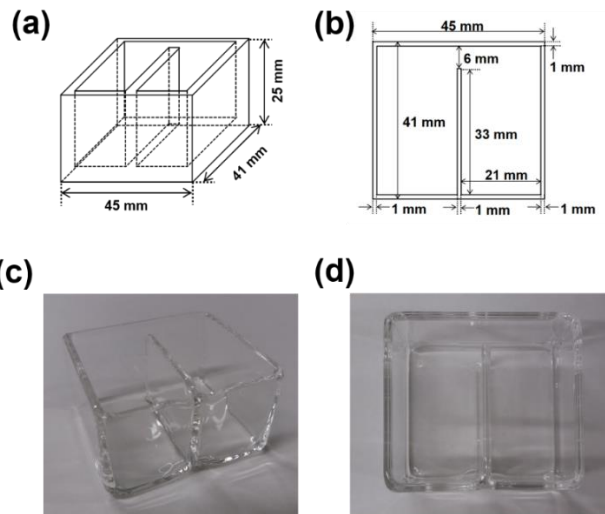
Figure S8. Custom-made U-shaped glass electrochemical cell. (a) and (b) Cell specifications. (c) and (d) Photographs of the cell.
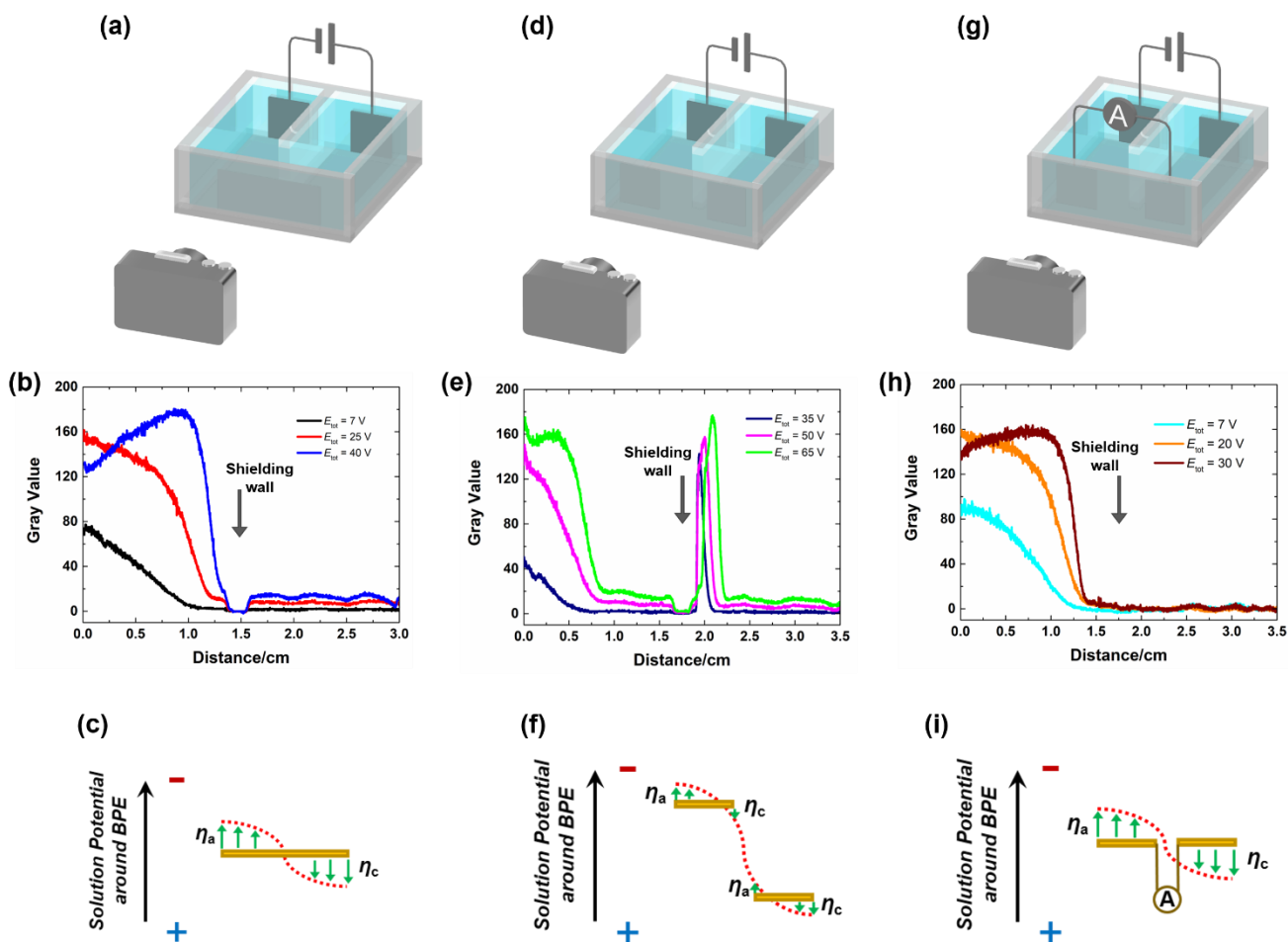
Figure S9. (a), (d) and (g) Experimental set-up for ECL imaging analysis for the U-shaped configuration. The ITO side was positioned to face the driving anode and cathode, while the ECL emission was recorded from the glass side through the camera positioned in front of the cell's wall where the BPE was leaned. Configuration (a) is for the U-shape configuration having only one single BPE (ITO 3 cm × 1 cm); configuration (d) is for two independent BPEs without any electrical connection in between; configuration (g) is for a s-BPE system realized when the electrical connection between the two plates of ITO is performed wiring the two ITOs outside the electrolytic solution using an ammeter (indicated as A letter). In both configurations (d) and (g) ITO plates were 1.5 cm × 1.5 cm of dimension. (b), (e) and (h) Two-dimensional ECL intensity profiles of the correspondent images reported in Figure 5. (c), (f) and (i) Expected potential profiles on the BPE surfaces for the U-shaped configuration; η_a and η_c symbols indicate the anodic and cathodic overpotential, respectively.
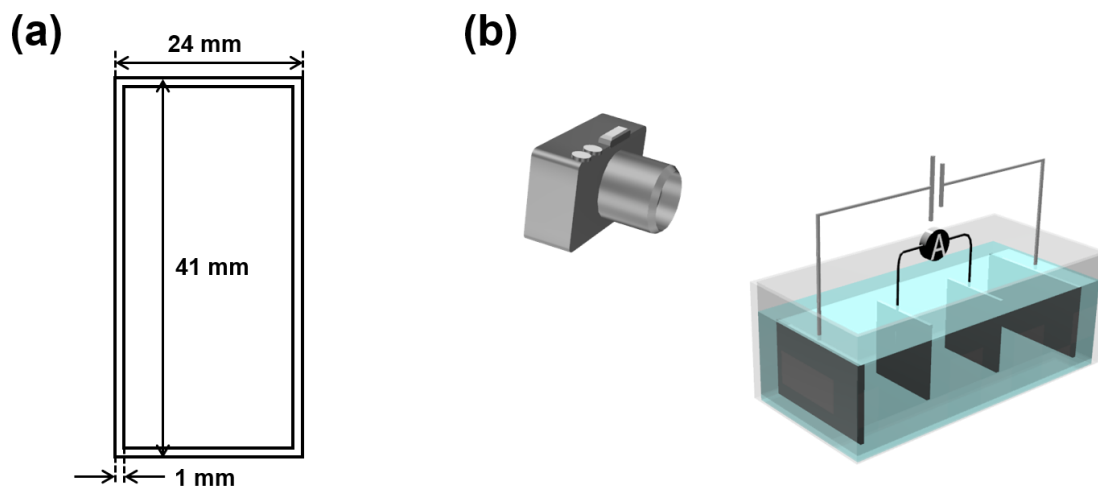
(a)

24 mm

41 mm

1 mm

(b)

Figure S10. (a) Rectangular electrochemical cell used for stacked bipolar electrolysis configuration studies. (b) Experimental set-up for ECL imaging analysis using this configuration. Pt driving electrodes were positioned at the walls of the cell, while two plates of ITO (1 cm × 1 cm) used as BPEs were placed in the middle of the cell and connected through an ammeter (indicated as A letter), obtaining a s-BPE system. Every ITO plate faced the corresponding driving electrode and the distance between the two BPEs was kept constant at 1 cm.

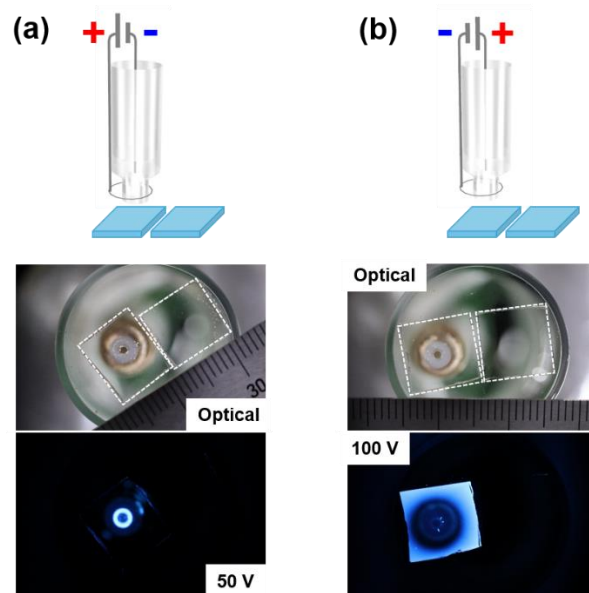**ECL imaging of cylinder configuration with two BPEs**

Figure S11. Photographs of ECL emission (luminol 10 mM and H_2O_2 30 mM in NaOH 0.1 M, pH 12.6) for the cylinder configuration with the cylinder positioned above one of the two BPEs. (a) Configuration having the driving cathode as inner electrode and the driving anode as outer electrode. Bottom part: optical image of two ITO plates (1 cm × 1 cm each) used as BPEs and correspondent ECL image for $E_{tot} = 50$ V. White dotted lines represent the position of the two BPEs. In configuration (b) the arrangement of the driving electrodes is opposite of configuration (a). Bottom part: optical image of two ITO plates (1 cm × 1 cm each) used as BPEs and correspondent ECL image for $E_{tot} = 100$ V. White dotted lines represent the position of the two BPEs.
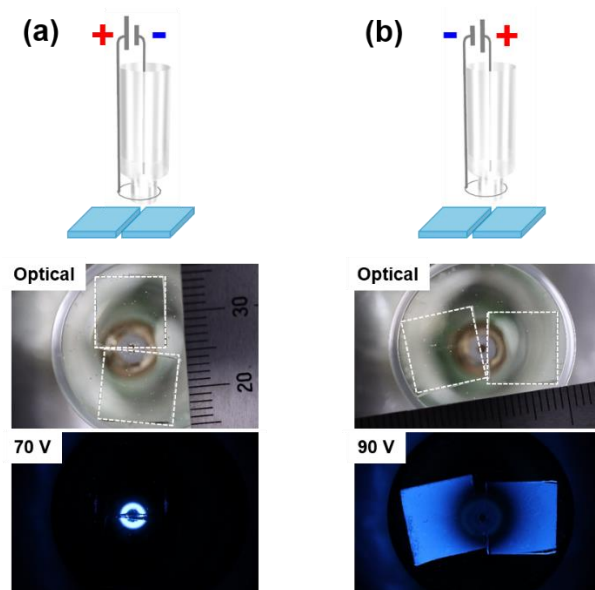
Figure S12. Photographs of ECL emission (luminol 10 mM and H_2O_2 30 mM in NaOH 0.1 M, pH 12.6) for the cylinder configuration with the cylinder positioned above the edges of two BPEs. (a) Configuration having the driving cathode as inner electrode and the driving anode as outer electrode. Bottom part: optical image of two ITO plates (1 cm × 1 cm each) used as BPEs and correspondent ECL image for E_{tot} = 70 V. White dotted lines represent the position of the two BPEs. In configuration (b) the arrangement of the driving electrodes is opposite of configuration (a). Bottom part: optical image of two ITO plates (1 cm × 1 cm each) used as BPEs and correspondent ECL image for E_{tot} = 90 V. White dotted lines represent the position of the two BPEs.

Measurements of current passing in the U-shaped configuration: bare *vs* insulated driving electrodes
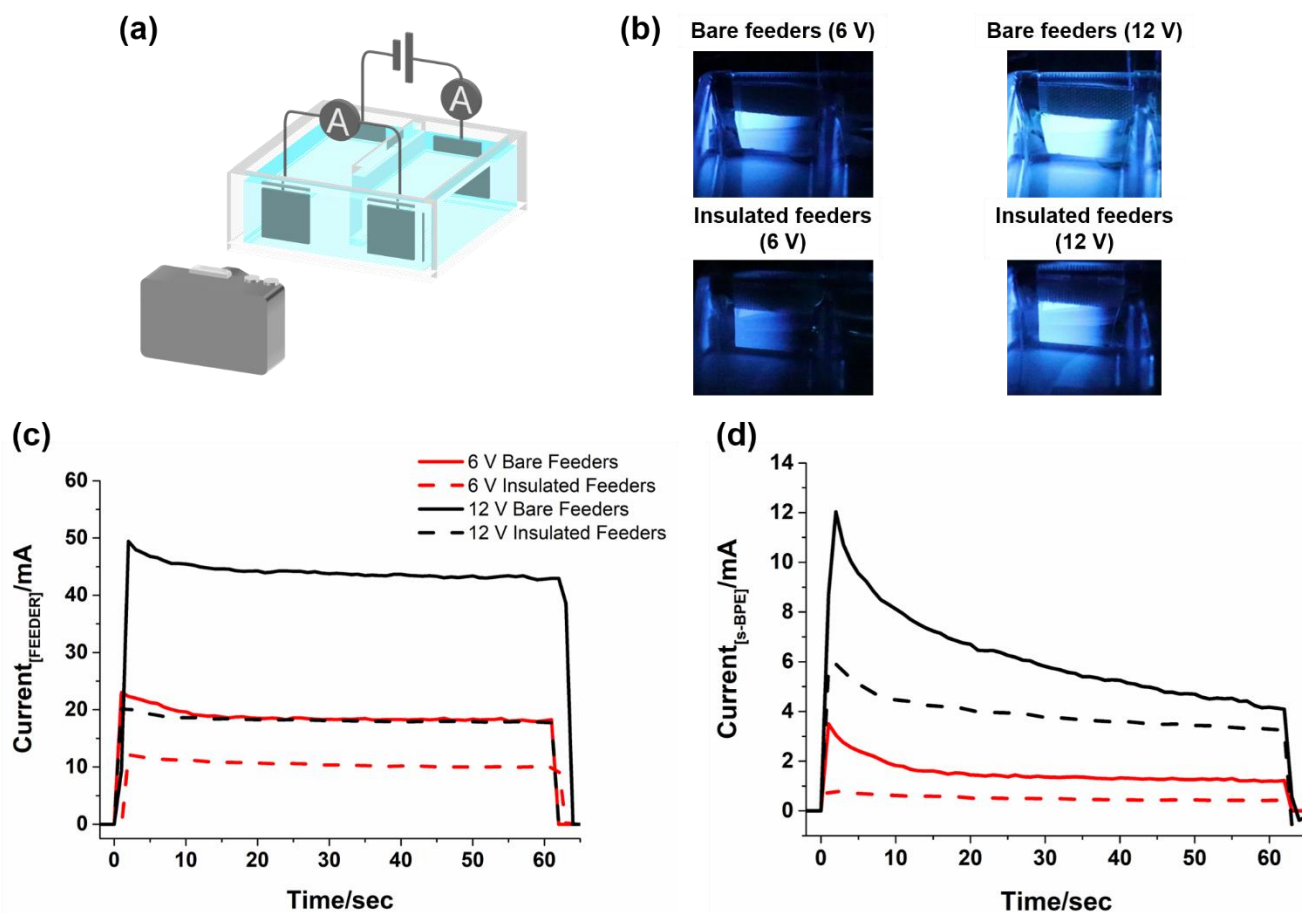

Figure S13. Measurements of current passing in the U-shaped configuration with s-BPE. (a) Experimental set-up for current measurements with simultaneous ECL imaging acquisition in the U-shape electrolytic cell; s-BPE was realized connecting two plates of ITO through an ammeter (indicated as A letter) positioned in series outside the electrolytic solution, while driving (feeder) electrodes were connected through an ammeter positioned in parallel outside the electrolytic solution. (b) Photographs of ECL emission (luminol 10 mM and H_2O_2 30 mM in NaOH 0.1 M, pH 12.6) of the anodic pole of an s-BPE (ITO plate 1.5 cm × 1.5 cm of dimension) positioned in the U-cell driven by a pair of bare driving electrodes (photographs in the upper part at 6 and 12 V) or by a pair of insulated driving electrodes (photographs in the bottom part at 6 and 12 V). (c) Measurement of current passing between driving electrodes and (d) through the s-BPE for $E_{tot} = 6$ V (red lines) and 12 V (black lines), having bare driving electrodes (solid lines) or insulated driving electrodes (dashed lines).

References:

(1) Duval, J.; Kleijn, J. M.; van Leeuwen, H. P. *J. Electroanal. Chem.* **2001**, *505*, 1–11.

(2) Duval, J. F. L.; Minor, M.; Cecilia, J.; van Leeuwen, H. P. *J. Phys. Chem. B* **2003**, *107*, 4143–4155.

(3) Mavré, F.; Anand, R. K.; Laws, D. R.; Chow, K.-F.; Chang, B.-Y.; Crooks, J. A.; Crooks, R. M. *Anal. Chem.* **2010**, *82*, 8766–8774.