Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Miniaturized Solid Salt Reverse Electrodialysis Battery: A Durable and Fully Ionic Power Source

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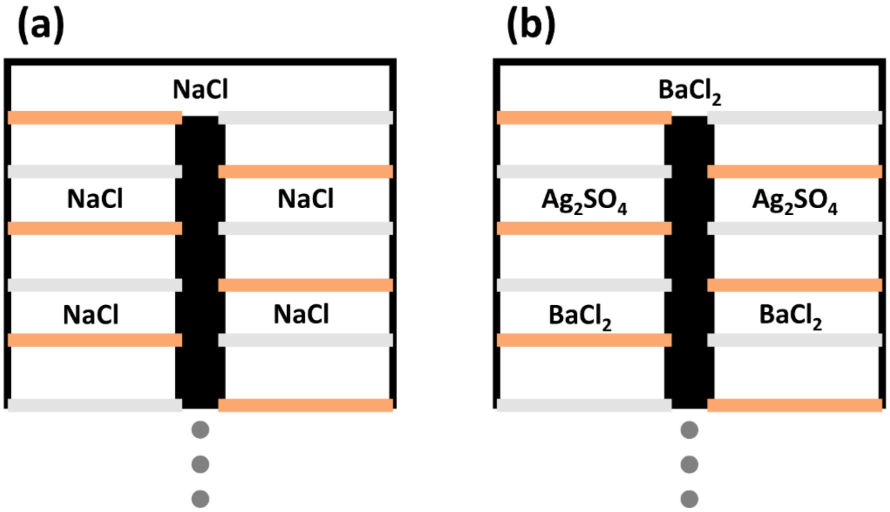


Fig. S1. Schematic diagram of (a) NaCl based ssRED (NssRED) and (b) $BaCl_2/Ag_2SO_4$ based precipitation-assisted ssRED (PssRED).

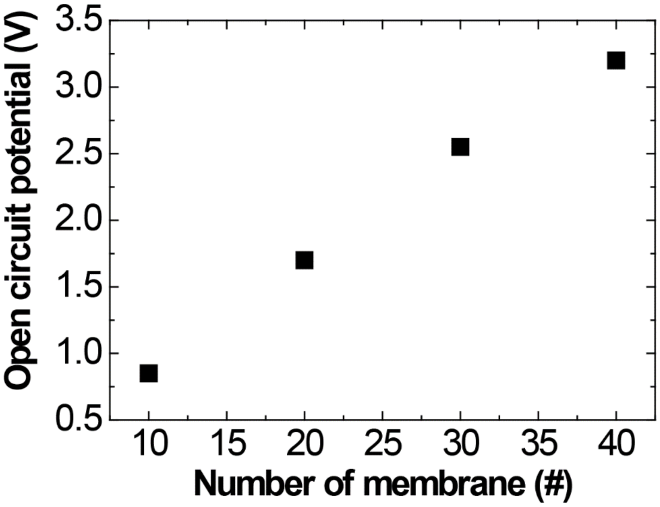


Fig. S2. Linear dependence of open circuit potential (OCP) versus number of PssRED stacks.

The charge that can be delivered by PssRED would be proportional to the initial salt loading as shown in **Figure S3**. With the same setup which had been used to obtain the internal resistance of RED, total charge was measured until the PssRED was completely discharged. 1, 3, 10, 30 mg of $BaCl_2$ salt and the same number of moles of Ag_2SO_4 salt were loaded, which is 1.5 times in mass. In this experiment, the solutions in HC chambers are not saturated because the experiment time would be too long when the solution is saturated. Water was refilled every couple of hour during the measurement. As the result shown below, the delivered charge has linear relationship to the amount of $BaCl_2$ salt, although a large deviation from the theoretical charge (0.93 C / 1 mg of $BaCl_2$) was observed.

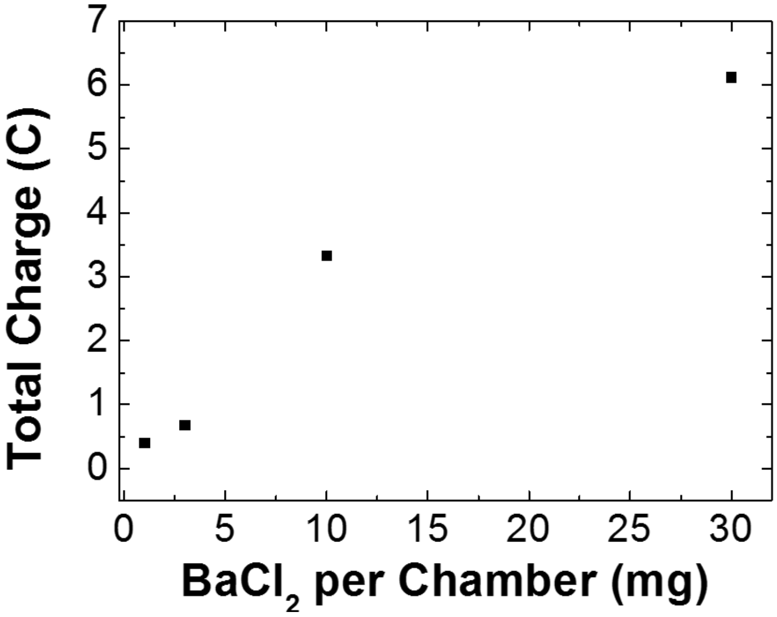


Fig. S3. Total Charge versus $BaCl_2$ amount per chamber

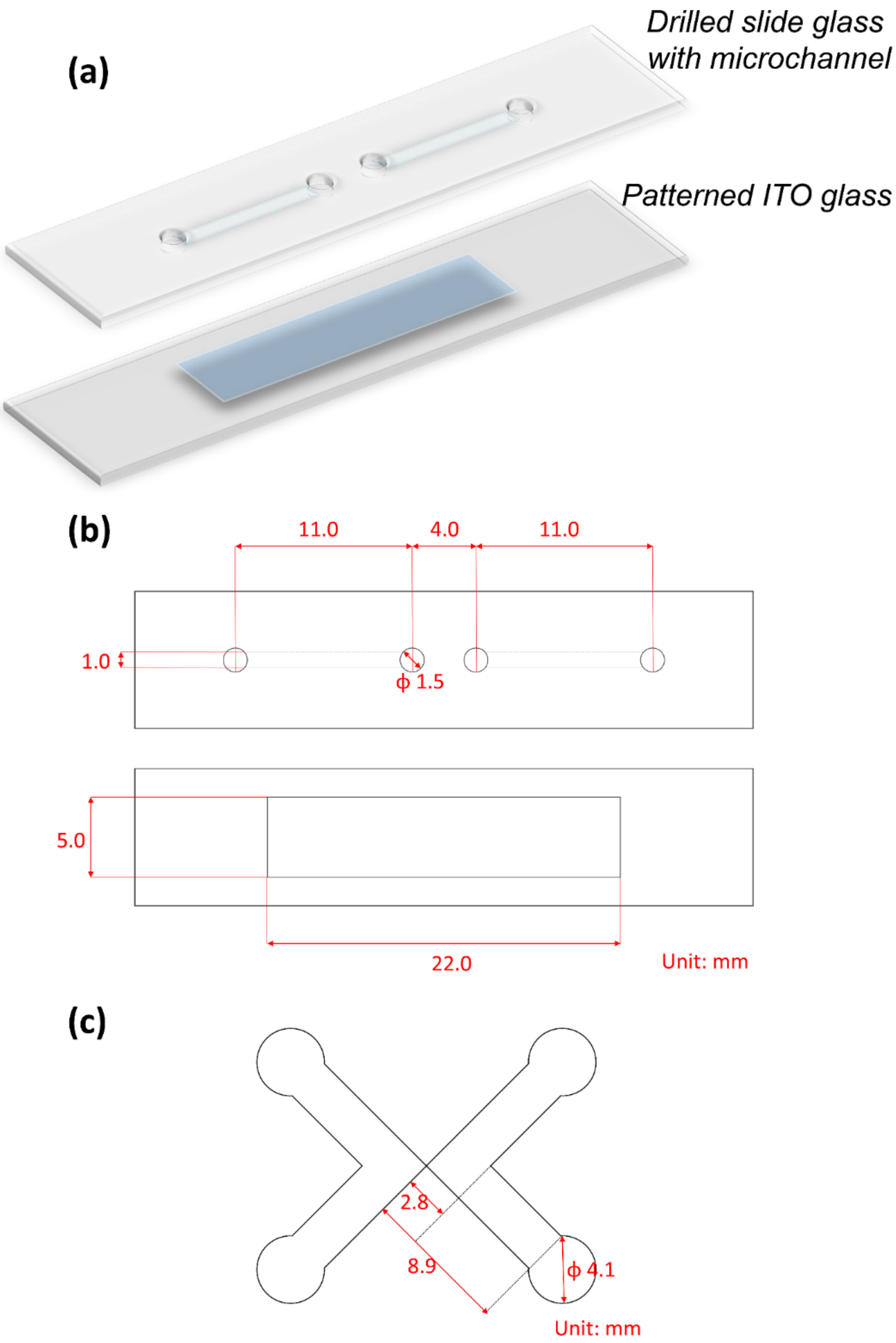


Fig. S4. (a) Schematic diagram of microchip for bipolar electrochemical analysis. (b) Dimensions of the upper and bottom glass slides of BPE. In the upper glass, 50 µm deep microchannel was etched and the inlet was drilled. For the bottom glass, indium tin oxide bipolar electrode of 5.0 mm × 22.0 mm dimensions was etched. These two glasses were attached by thermal bonding. (c) Dimensions of X-shaped diode chip glass slide. 40 µm deep microchannel was etched.

In **Figure S5**, we presented individual cyclic voltammograms of aqueous 5 mM $Ru(bpy)_3^{2+}$-25 mM tripropylamine (TPrA), 1 mM BV, and 50 mM H_2O_2 solution, acquired on an ITO coated glass electrode against the Ag/AgCl reference electrode stored in 3 M NaCl solution. For the $Ru(bpy)_3^{2+}$ and TPrA system, TPrA serves as a single electron reductant that undergoes single electron transfer to pre-oxidized $Ru(bpy)_3^{3+}$ or the electrode itself.

$\mathrm{Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^-}$

$\mathrm{Ru(bpy)_3^{3+} + Pr_3N \rightarrow Ru(bpy)_3^{2+} + Pr_3N^{\cdot+}}$

$\mathrm{Pr_3N^{\cdot+} \rightarrow Pr_2N\dot{C}HEt + H^+}$

$\mathrm{Ru(bpy)_3^{3+} + Pr_2N\dot{C}HEt \rightarrow Ru(bpy)_3^{2+*} + Pr_2N^+{=}CHEt}$

$\mathrm{Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+}} + hv$

(where $\mathrm{Pr = CH_3CH_2CH_2}$- and $\mathrm{Et = CH_3CH_2}$-)

In this process, excited $Ru(bpy)_3^{2+}*$ is formed, which rapidly relaxes to the ground state, generating orange ECL signals at 630 nm at the potential higher than 0.9 V (Blue curve in **Figure S5**).[1] Moreover, BV^{2+} and H_2O_2 showed reduction onset potentials respectively at −0.4 V and −0.2 V (solid red and dashed red). Therefore, the cyclic voltammograms show that the minimum potential for bipolar-ECL detection of the analytes is ~1.3 V and ~1.1 V for BV and H_2O_2, respectively. The necessary potential difference at driving electrodes could be calculated from equation 1, where ΔE_{elec} is effective potential difference, ΔE_{tot} is potential difference at driving electrodes, l_{elec} is BPE length and $l_{channel}$ is channel length.

$$\Delta E_{elec} = \Delta E_{tot} \times (l_{elec}/l_{channel}) \qquad (1)$$

Using the values, l_{elec} (=1.65 cm) and $l_{channel}$ (=1.90 cm), the calculation provided the necessary ΔE_{tot} as ~1.5V and ~1.3V respectively for BV and H_2O_2. In order to facilitate overcoming the overpotential and obtaining a detectable intensity of ECL, a practical value of 2.3 V was chosen (ΔE_{elec}=2.0 V).

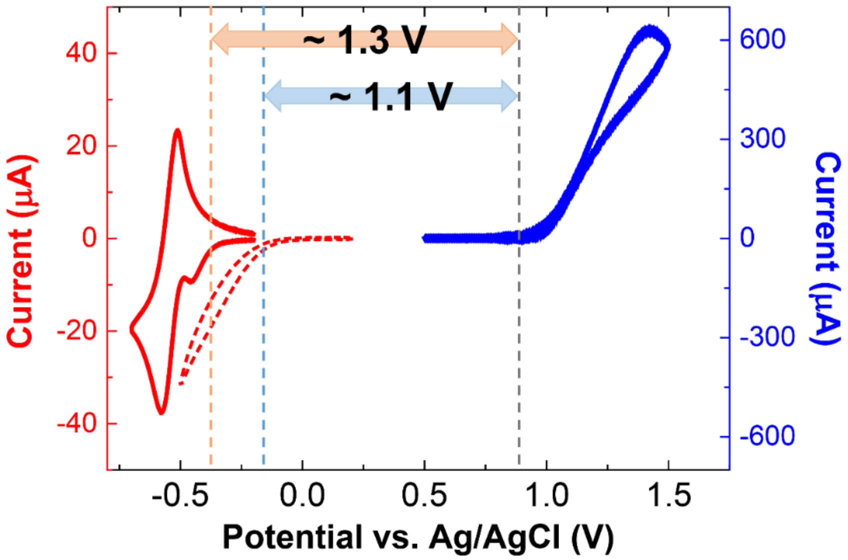


Fig. S5. Cyclic voltammograms of 1 mM benzyl viologen (solid red), 50 mM hydrogen peroxide (dashed red) and 5 mM tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate with 25 mM tripropylamine solution (dashed red). All the solutions were made in pH 6.9 PBS. Potential required for bipolar electrochemical analysis was 1.3 V and 1.1 V for benzyl viologen and hydrogen peroxide, respectively.

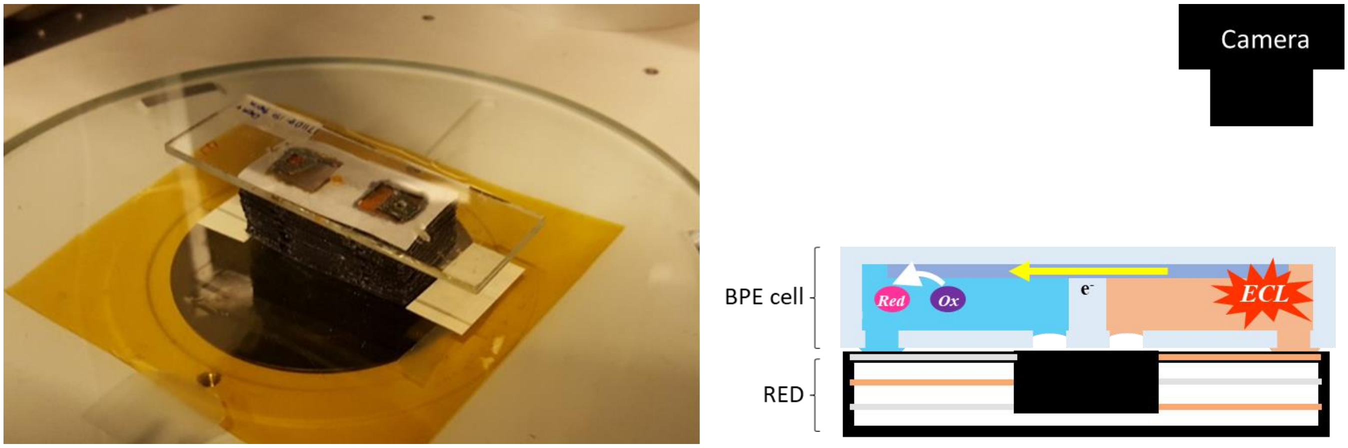
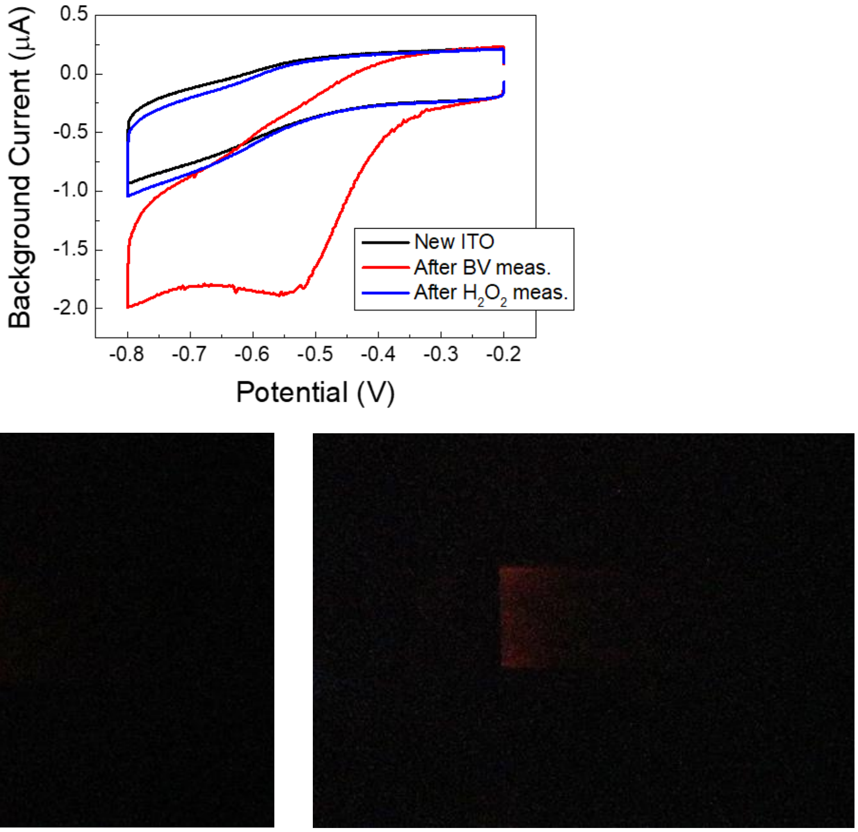


Fig. S6. Photograph and Schematic Diagram of PssRED in Contact with ECL Sensing System

As shown in the cyclic voltammogram in **Figure S7** (conducted after N_2 gas purging), after BV measurement, the ITO electrode shows significantly increased background current while the ITO electrode after H_2O_2 measurement shows nearly identical cyclic voltammogram. Evidently, after ECL measurement of BV, even with thorough washing process, the BPE chip exhibited larger blank ECL signal compared to that of a bare, clean BPE chip. We attribute this result to adsorption of BV onto the ITO electrode.



Blank ECL

Blank ECL after ECL measurement of BV

Fig. S7. Cyclic voltammogram and ECL of ITO electrodes, bare and after measurement of BV.

Figure S8a and **Figure S8c** show the clear dependence of current on the concentration of analytes when the potential is applied by a commercial potentiostat. The intensity of ECL from the detecting channel also displays a concentration dependence (**Figure S8b** and **Figure S8d**).

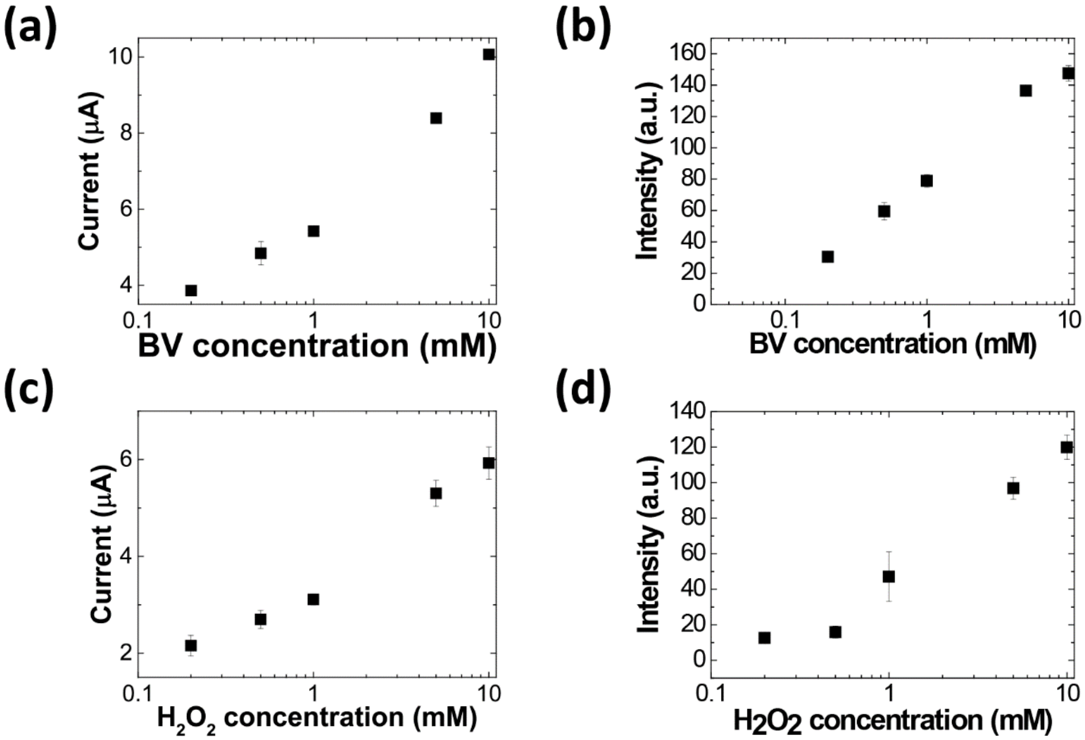


Fig. S8. Current sampled 15 seconds after bias and ECL intensity of bipolar electrochemical system with varying the concentration of analytes. Bias of 2.3 V was applied by commercial potentiostat (Compactstat, Ivium). Reporting channel: 5 mM $Ru(bpy)_3Cl_2$ and 25 mM TPA. (a, b) Detecting channel: 0–10 mM BV. (c, d) Detecting channel: 0–10 mM H_2O_2. Applied potential is 2.3V. All the solutions were made in pH 6.9 phosphate buffer solution.

Reference

1 Y. Zu and A. J. Bard, *Anal. Chem.*, 2000, **72**, 3223.