Supplementary Information

Achieving Low Voltage Half Electrolysis with a Supercapacitor Electrode

Chuang Peng*, Di Hu, and George Z. Chen*

Experimental Methods and Calculations

1. Electrode and Electrolytic Cell for electrodeposition of polypyrrole

Titanium sheet (Advent, thickness 0.1 mm) was cut into 2×2 cm squares with a tail for electric connections (Fig.S1 and Fig.S3A). Prior to use, the Ti electrode was polished with sand paper and rinsed with acetone and deionised water several times. The CMPB modified Ti electrode was prepared by casting 120 µL aqueous suspension of CMPB (10 mg/mL) and PTFE (1.5 mg/mL) on Ti plates placed on a hot plate heated at 80 ℃. The sampling was carried out with a micro-pipette, while the CMPB-PTFE suspension was kept in a glass vial immersed in an ultrasound bath to ensure a uniform dispersion of solid particles.

The electrolyser was fabricated by placing a rubber U housing between two electrodes to form the electrolyte container (Fig.S1). The wall thickness of the U housing was 0.4 cm, so the effective electrode area for electrolysis was $(2 – 0.4\times2)^2 = 1.44$ cm^2. The Ti plates and U housing were sandwiched between two Perspex supporting plates and the whole electrolyser was tightened and sealed by means of stainless steel screws.

In all the three electrode experiments, an Ag/AgCl in 3.0 mol/L KCl (aqueous) half-cell was used as the reference electrode, and a coiled platinum wire was the counter electrode. In Fig.1A, the Ti working electrode was a 0.5 cm square Ti plate with one side covered by epoxy. The CMPB electrode was prepared by casting 10 mL of the aforementioned CMPB-PTFE suspension on the Ti spade electrode.

The electrowinning of copper was conducted on a CHI660D electrochemical workstation. The rest of the electrochemical experiment was conducted on a PGSTAT30 Autolab Potentiostat.

2. Capacitance Calculation

In Fig.1A, CMPB exhibited a plateau CV current in a broad potential range, its capacitance was calculated from

$$C = I/\upsilon \tag{4}$$

where υ is the potential scan rate, and I is the discharge capacitive current (negative plateau current), 0.21 mA at the potential of 0.0 V.

The CV of the electro-deposited PPY (Fig.S4B) does not have a current plateau and the current varies with potential due to its pseudocapacitive nature. Therefore, the capacitance of PPY was calculated from the electric charge instead of the CV current, using

$$C = Q/(2*U) \tag{5}$$

where Q is the total electric charge of the positive and negative scan, U is the CV potential cycling range (-0.2 to 0.5 V).

3. Calculation of the energy consumption during galvanostatic electrolysis

The voltage-time curves of galvanostatic electrolysis in Fig.2B and Fig.S3 were recorded at a time interval of 0.2 second. Therefore, the electrical energy was actually calculated by the sum of the energy consumed at each time interval:

$$W = \Sigma\, I(U_{i+1}+U_i)\, \Delta t/2 \tag{6}$$

4. Copper electrowinning

High purity (99.99%, Advent Research Materials) copper and lead sheets were cut into 2 × 2 cm squares. One side of the electrodes is covered with polypropylene adhesive tape. The supercapacitor electrode was prepared by casting CMPB and PTFE aqueous suspension on the lead electrode. The loading of CMPB was 5mg. The electrowinning was carried out in an aqueous solution of 40 g/L $CuSO_4$ and 150 g/L H_2SO_4 at ambient temperature of 20°C. So the Cu^{2+} concentration was 0.25mol/L. Magnetic stirring was used to improve the mass transport.

5. Energy consumption in copper electrowinning

The cell potential of the copper electrowinning with oxygen evolution as the anode process is calculated using the Nernst equation.

$$
\begin{aligned}
E_{rxn} \quad &= E_{rxn}{}^0 - RT*\ln Q/zF \\
&= 0.337\text{-}1.229 - 8.314*293*\ln(1/[Cu^{2+}])/(2*96485) \\
&= -\,0.892\text{-}\,0.0126*\ln(1/0.25) \\
&= -0.892\text{-}\,0.017 \\
&= -\,0.909\ \text{V}
\end{aligned}
$$

Therefore, the Gibbs free energy change

$$
\begin{aligned}
\Delta G &= -nFE_{rxn} \\
&= -2*96485*(-0.909) \\
&= 175409\ \text{J/mol}
\end{aligned}
$$

At 100% efficiency, i.e., with 100% current efficiency, neglecting any activation loss, ohmic loss or concentration loss, the energy consumption per kg copper is calculated as 175409*1000/64 = 2740765 J, or 0.761 kWh.

During the electrolysis in Fig. 3, the mass of deposited copper is calculated by the Faraday's law, assuming a current efficiency of 95% for both processes.

$$m = MIt/zF*95\% = 64*0.002*100/(2*96485)*0.95 = 6.3\times10^{-5}\text{g}$$

The energy consumption is calculated by integration of the voltage curves (Equation 6, time interval 0.01s) as 0.287 and 0.110 J, for the conventional and half electrolysis respectively. Therefore, the energy consumption were 1.265 and 0.485 kWh/kg Cu.
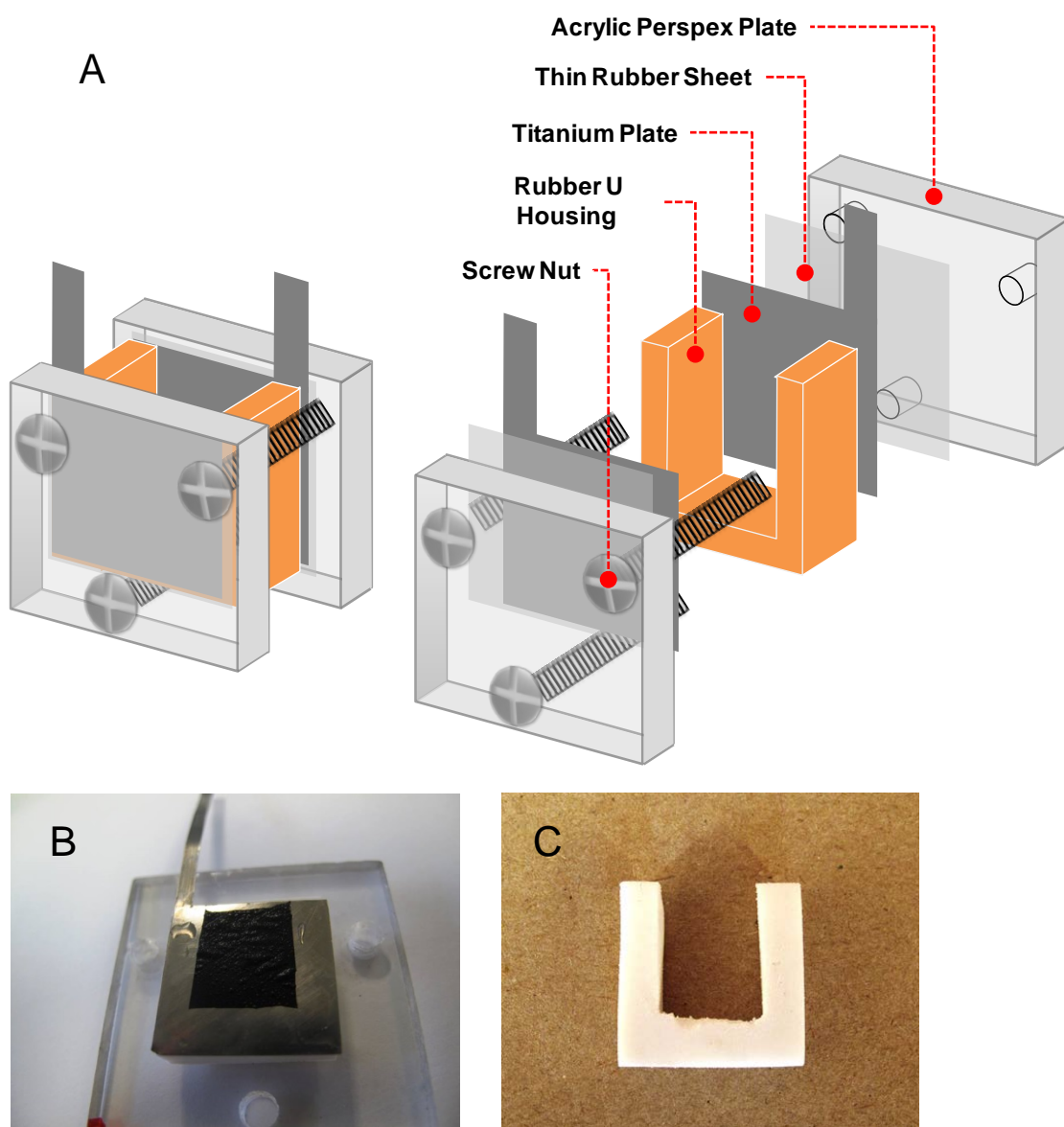
Figure S1. (A) Schematic illustrations of the electrolytic cell. Digital photograph of Ti electrode mounted on top of rubber sheet and Perspex supporting plate (B) and a rubber U housing (C).
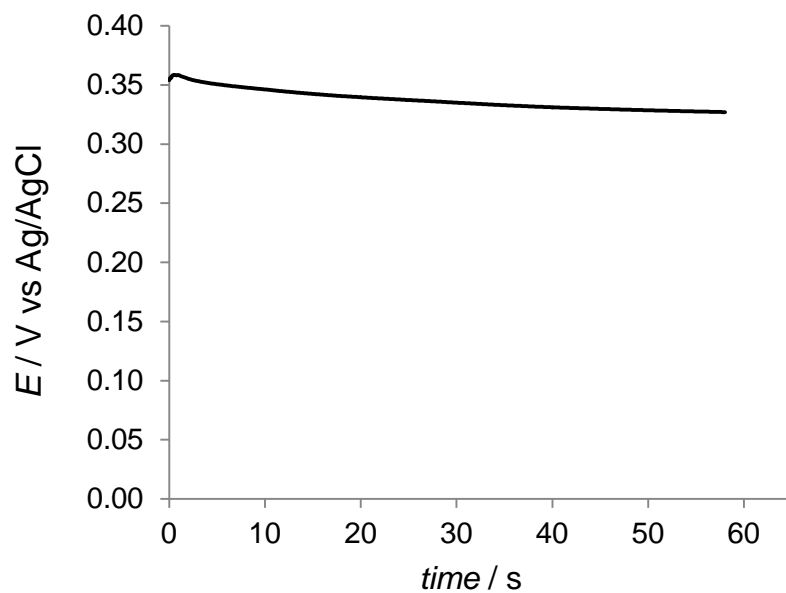
Figure S2. Open circuit potential (OCP) of the freshly prepared CMPB electrode, measured prior to the galvanostatic electrolysis in Fig.2B.
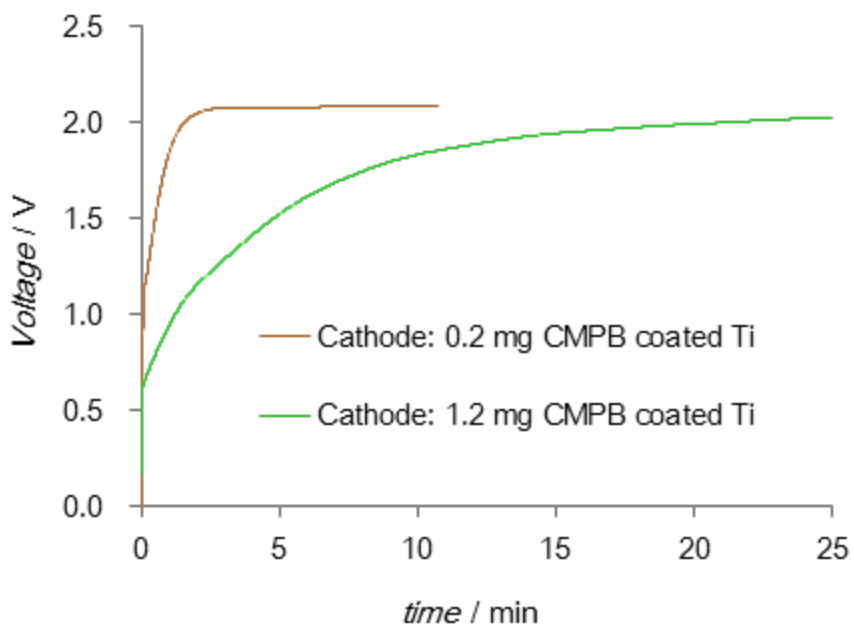
Figure S3. Voltage-time curves of galvanostatic electrolysis with Ti anode and Ti cathode modified with 0.2 and 1.2 mg CMPB. Applied DC current: 1 mA. Electrolyte: 0.5 M KCl and 0.25 M pyrrole aqueous solution.
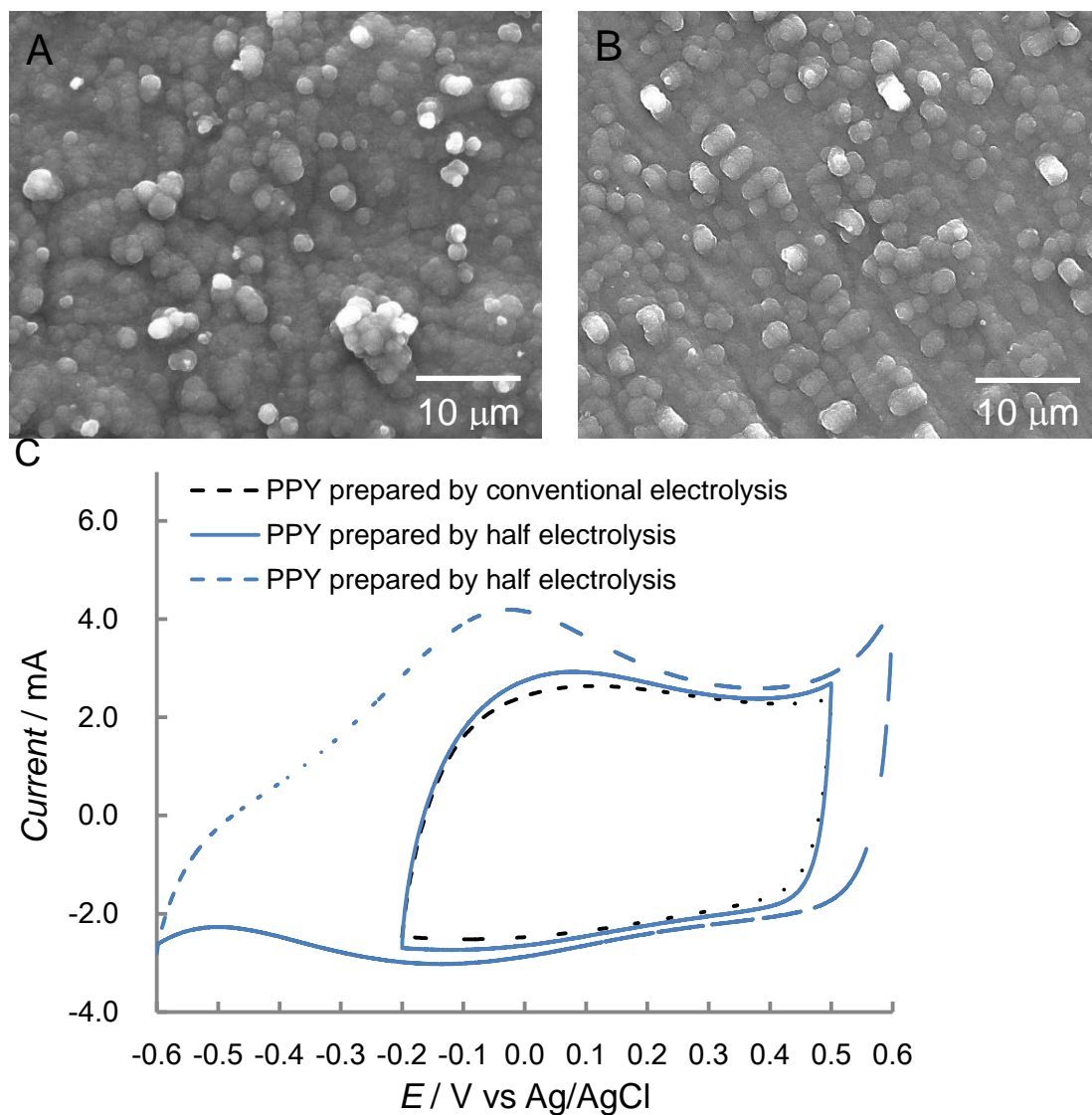
Figure S4. SEM images of PPY prepared by conventional (A) and half (B) electrolysis. (C) Cyclic voltammograms of PPY prepared by conventional and half electrolysis. Electrolyte: 0.5 M KCl aqueous solution. Potential scan rate: 20 mV/s. All the PPY films were deposited by galvanostatic electrolysis at a current of 1 mA for 1500 seconds.
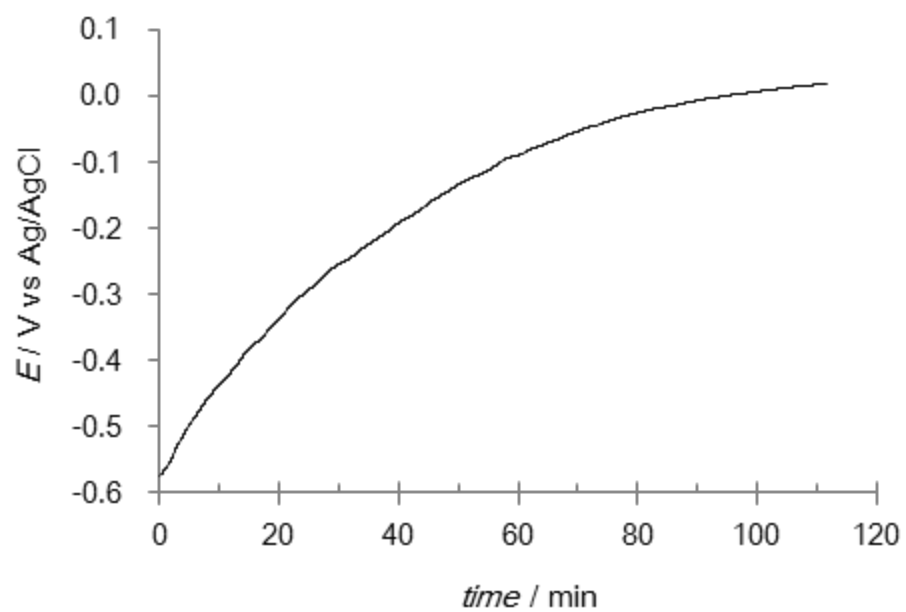
Figure S5. The open circuit potential (OCP) – time plot of the CMPB modified Ti electrode after the galvanostatic electrolysis (Fig.2B).
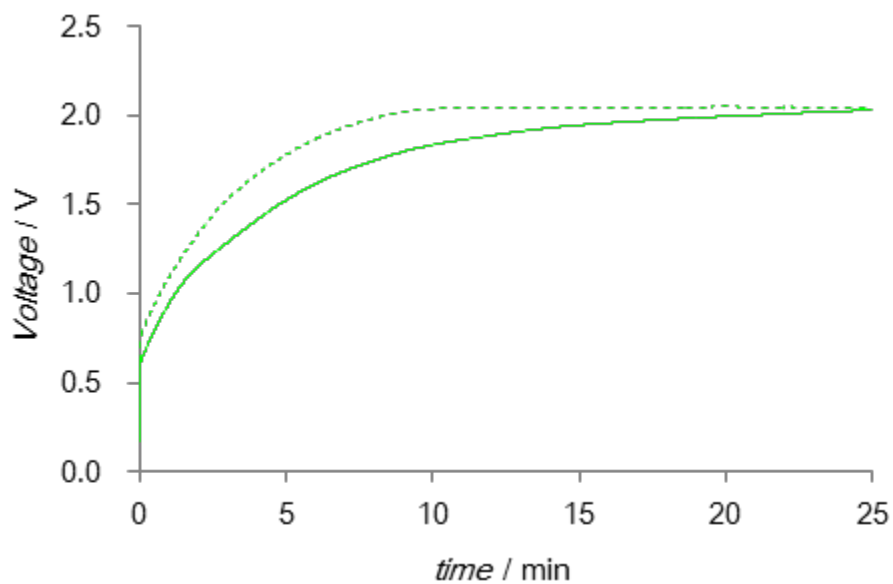
Figure S6. Voltage-time curves of galvanostatic electrolysis with a freshly made 1.2 mg CMPB modified Ti cathode (solid line) and the same cathode after the potential relaxation in Fig.S4 (dashed line). Applied DC current: 1 mA. Electrolyte: 0.5 M KCl and 0.25 M pyrrole aqueous solution.
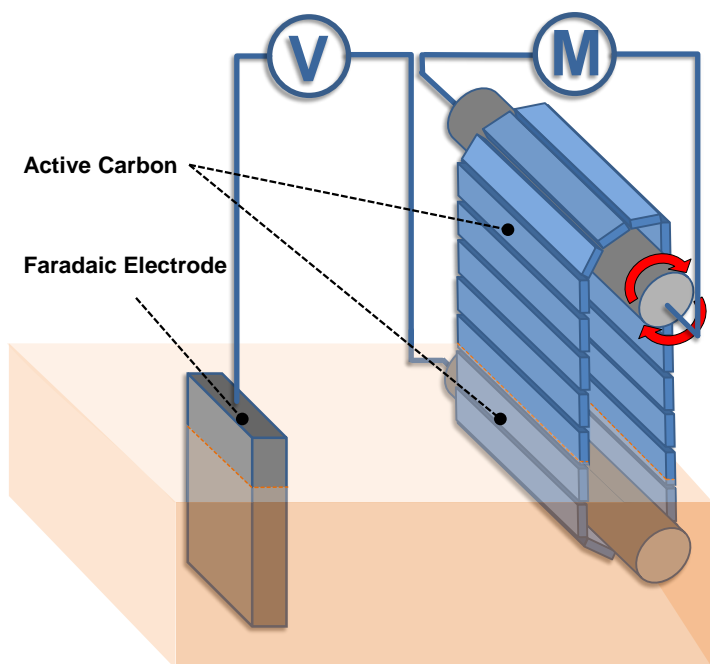
Figure S7. Schematic illustration of a half electrolysis cell with a moving conveyor belt electrode.
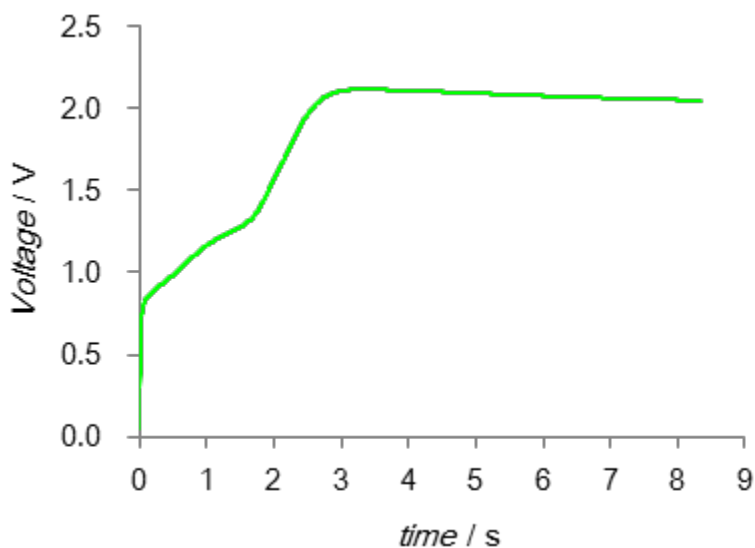
Figure S8. Voltage-time curve of galvanostatic electrolysis with a Ti anode and PPY modified Ti cathode. Applied DC current: 0.5 mA. Electrolyte: 0.5 M KCl and 0.25 M pyrrole aqueous solution. The PPY modified Ti cathode was prepared by galvanostatic electrolypolymersiation at 1.0 mA for 750 s.

Table S1. Summary of the electrical energy consumption in Cell 2 and Cell 3 during different time periods of the galvanostatic electrolysis. Calculated from Fig.2B and Fig.S3. Cathode of Cell 3: 0.2 mg CMPB modified Ti.

Time duration / min	0-0.5	0.5-1	1-5	5-10
$W_{Cell\,3}$ (mJ)	62.3	65.2	518.0	645.0
$W_{Cell\,2}$ (mJ)	35.1	50.5	492.2	624.9
$W_{Cell\,2}$: $W_{Cell\,3}$ ×100%	56.3%	77.5%	95.0%	96.9%