# **Journal Name**

# ARTICLE



# **Supporting Information for**

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

# Thermo-electrochemical Cells Empowered by Selective Inclusion of Redox-active Ions by Polysaccharides

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Thermo-electrochemical cells (TECs) are a class of thermoelectric materials that offer high thermoelectric voltage (Seebeck coefficient) with potentially lower costs compared to the conventional thermoelectric materials. To maximize the potential of TECs, polymer-ion interactions are introduced to increase the Seebeck coefficient with a redox pair of I<sup>-</sup>/I<sub>3</sub><sup>-</sup>. Starch and polyvinylpyrrolidone (PVP) are employed as polymeric hosts for  $I_3^-$  ions. The effective concentration of free  $I_3^-$  ions in the cold cell decreases due to their selective inclusion in polymers, resulting in higher  $[1^-]/[1_3^-]$  ratio. Meanwhile, at a higher temperature, the inclusion of  $I_3^-$  ions by the polymeric host becomes less effective, and the ratio of  $[I^-]/[I_3^-]$  decreases. Consequently, the two electrode cells differing in temperature show a considerable concentration difference of I<sub>3</sub><sup>-</sup> ions, and the Seebeck coefficient increased up to 1.5 mVK<sup>-1</sup>. Among these polymer TECs, starch showed notable performance with the increase in Seebeck coefficient and output power by factor а of two.

# S1. Details of the experimental procedures

#### S1.1 Sample preparations of A ( $[KI]_0 = 12.5 \text{ mM}$ , $[I_2]_0 = 2.5 \text{ mM}$ ) with Starch

KI (2.49 g, 15 mmol, Wako Pure Chemical Industries) and  $I_2$  (1.27 g, 5 mmol, Chameleon Analytical Reagent) were dissolved into deionized water (100 mL of total volume) to produce an aqueous solution **1** ( $[KI]_0 = 150$  mM,  $[I_2]_0 = 50$  mM). KI (0.83 g, 5 mmol) was dissolved in water (50 mL) to produce another aqueous solution of KI (0.1 M). Refined potato starch (2.43 g, 15 mmol in glucose unit, Wako) was dissolved in hot water (70 °C, 25 mL) to produce an aqueous solution of starch (0.6 M). The aqueous solution of starch (0.6 M) was diluted to produce 0.3 M aqueous starch solution. These aqueous starch solutions (0.3 or 0.6 M), KI (0.1 M) and solution **1** listed in Table S1 were mixed together and messed up to 50 mL with water. The final concentration of starch is shown in the chart.

Table S1. Su	mmary of samp	le preparations.			
No.	starch <sub>aq</sub>	Solution <b>1</b>	0.1 M	Starch	Total
	(mL)	(mL)	Kl <sub>aq</sub> (mL)	(mM)	(mL)
1	1.0 <sup>[a]</sup>	2.5	2.5	6	50
2	2.5 <sup>[a]</sup>	2.5	2.5	15	50
3	5.0 <sup>[a]</sup>	2.5	2.5	30	50
4	10 <sup>[a]</sup>	2.5	2.5	60	50
5	15 <sup>[a]</sup>	2.5	2.5	90	50
6	25 <sup>[b]</sup>	2.5	2.5	300	50

[a] 0.3 M [b] 0.6 M

#### S1.2 Sample preparations of A ( $[KI]_0 = 12.5 \text{ mM}$ , $[I_2]_0 = 2.5 \text{ mM}$ ) with PVP

PVP K-30 (320 mg, 2.88 mmol in the monomer unit, M.W. = 40,000, Chameleon Reagent) was dissolved into water (20 mL) to produce an aqueous solution of PVP (0.144 M). 0.5 M aqueous PVP solution was separately prepared by dissolving 555 mg (5 mol) of PVP into water (10 mL). Those aqueous solutions of PVP (0.14 M/0.5 M), KI (0.1 M) and solution **1** listed in Table S2 were mixed and messed up to 50 mL with water. The final concentration of PVP is shown in the chart.

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Table S2. Sui	mmary of samp	le preparations.			
No. $PVP_{aq}$ Solution 1 $0.1$ M $PVP$ Iotal           (mL)         (mL)         (mL)         Kl <sub>aq</sub> (mL)         (mM)         (mL)           1 $1.25^{[a]}$ $2.5$ $2.5$ $3.6$ $50$ 2 $6.25^{[a]}$ $2.5$ $2.5$ $18$ $50$ 3 $12.5^{[a]}$ $2.5$ $2.5$ $36$ $50$ 4 $1.0^{[b]}$ $2.5$ $2.5$ $10$ $50$ 5 $7.2^{[b]}$ $2.5$ $2.5$ $72$ $50$		21/2			0.10	
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	NO.	PVPaq	Solution 1	0.1 M	PVP	Total
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		(mL)	(mL)	Kl <sub>aq</sub> (mL)	(mM)	(mL)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	1.25 <sup>[a]</sup>	2.5	2.5	3.6	50
3         12.5 <sup>[a]</sup> 2.5         2.5         36         50           4         1.0 <sup>[b]</sup> 2.5         2.5         10         50           5         7.2 <sup>[b]</sup> 2.5         2.5         72         50	2	6.25 <sup>[a]</sup>	2.5	2.5	18	50
4         1.0 <sup>[b]</sup> 2.5         2.5         10         50           5         7.2 <sup>[b]</sup> 2.5         2.5         72         50	3	12.5 <sup>[a]</sup>	2.5	2.5	36	50
5 7.2 <sup>[b]</sup> 2.5 2.5 72 50	4	1.0 <sup>[b]</sup>	2.5	2.5	10	50
	5	7.2 <sup>[b]</sup>	2.5	2.5	72	50

[a] 0.14 M [b] 0.5 M

#### S1.3 Sample preparations of B ([KI]<sub>0</sub> = 100 mM, [I<sub>2</sub>]<sub>0</sub> = 2.5 mM) with Starch

KI (6.64 g, 40 mmol) and  $I_2$  (0.254 g, 1 mmol) were dissolved into deionized water (100 mL) to produce an aqueous solution **2** ([KI]<sub>0</sub> = 400 mM,  $[I_2]_0 = 10$  mM). The aqueous solution of starch (0.6 M) was prepared in the same method explained in Chapter 1-1, and 0.06 M of aqueous starch solution was prepared by the dilution. Those aqueous starch solution (0.06 M/0.6M) and solution **2** listed in Table S3 were mixed and messed up to 5 mL with water.

No.	Starch <sub>aq</sub> (mL)	Solution <b>2</b> (mL)	Starch (mM)	Total (mL)
1	0.50 <sup>[a]</sup>	1.25	6	5
2	1.25 <sup>[a]</sup>	1.25	15	5
3	2.5 <sup>[a]</sup>	1.25	30	5
4	0.5 <sup>[b]</sup>	1.25	60	5
5	2.5 <sup>[b]</sup>	1.25	300	5

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#### S1.4 Sample preparations of B ( $[KI]_0 = 100 \text{ mM}, [I_2]_0 = 2.5 \text{ mM}$ ) with PVP (Molecular weight 40,000)

PVP K-30 and solution 2 listed in Table S4 were mixed and messed up to 5 mL to give the final solution.

Table S4	. Summary	of sample	preparations.
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No.	PVP (mg)	Solution <b>2</b> (mL)	PVP (mM)	Total (mL)
1	5.0	1.25	9	5
2	10	1.25	18	5
3	20	1.25	36	5
4	40	1.25	72	5

#### S1.5 Sample preparations of B ( $[KI]_0 = 100 \text{ mM}$ , $[I_2]_0 = 2.5 \text{ mM}$ ) with PVP (Molecular weight 1300,000)

PVP K-85-95 (400 mg, 3.6 mmol in monomer unit, M.W. = 1,300,000, Acros Organics) was dissolved into water (25 mL) to produce an aqueous solution of PVP (0.144 M). The solution of PVP (0.14 M), solution **2** ( $[KI]_0$  = 400 mM,  $[I_2]_0$  = 10 mM) listed in Table S5 were mixed together and messed up to 25 mL with water. The final concentration of PVP is shown in the table.

Table S5. Summary of sam	ble S5. Summary of sample preparations.					
No.	PVP <sub>aq</sub> (mL)	Solution 2 (mL)	PVP (mM)	Total (mL)		
1	1.56	6.25	9	25		
2	3.13	6.25	18	25		
3	6.25	6.25	36	25		
4	12.5	6.25	72	25		

#### S1.6 Settings of H-cell

H-cell was used for the evaluation of  $V_{oc}-\Delta T$  plot for Seebeck coefficient, I–V and P–V curves (Fig. S1). Platinum wires with mesh were used as the electrode. The mesh increases the surface area of the electrodes, which is especially important for I–V and P–V measurements. The stirrer was used to stabilize the temperature in the half cell. The temperature inside the cell were monitored by thermometer (AS ONE, TM201). b) Photograph of H-cell. Sample: [KI]<sub>0</sub> = 12.5 mM, [I<sub>2</sub>]<sub>0</sub> = 2.5 mM, [KCI] = 2.0 M. 32 mL of the solution was introduced into each cell.



Figure S1. (a) Schematic illustration of H-shape cell (H-cell). (b) Photograph of H-shape cell.



Figure S2. The detailed structure of H-cell. A sample solution is put into the cell, and the liquid level is at the chain line. The left side of the cell is cooled at  $T_c$ , while the right side is heated at  $T_h$ .

Heat flows from the right to the left. At an equilibrium state, the heat flow is given by Fourie's law:

$$Q = \kappa A \frac{\Delta T}{\Delta x}$$

 $\kappa$  is heat conductivity of the sample solution, A is the cross-sectional area of the connecting tube (shown in gray zone),  $\Delta x$  is the length between heated and cooled sides, and  $\Delta T = T_h - T_c$ .

The inner resistance of the cell follows Ohm's law:

$$R = \frac{\Delta x}{\sigma A}$$

σ is ionic conductivity of the sample solution. Thus, larger cross-sectional area decreases the resistance of the cell, while it increases heat flow in the cell.

Values of those parameters when the volume of the solution in the cell is 32 mL are as follows:  $d = 20 \text{ mm}, \Delta x = 74 \text{ mm}, h = 4 \text{ mm}, A = 69 \text{ mm}^2, Q = 18 \text{ mW}$  at  $\kappa = 0.58 \text{ W}$  m<sup>-1</sup> K<sup>-1</sup>,  $\Delta T = 33 \text{ K}$ .

# S1.7 Settings of Mini-cell



**Figure S3.** Photographs of the miniature cell (Mini-cell). Fig. S3a: Mini-cell was used only for the evaluation of Voc– $\Delta$ T line (Seebeck coefficient). Two glass vials (Maruemu No.02, 2.2 mL) were connected by Teflon tube (inner diameter: 1 mm) into which the solution can flow. A platinum wire was used as the electrode (diameter: 0.5 mm). The temperature was evaluated by thermometer. Sample: [KI]0 = 2 mM, [I2]0 = 1 mM. Volume of the solution: 1.5 mL. Fig. S3b The solution turned blue after an addition of starch. Sample: [KI]0 = 2 mM, [I2]0 = 1 mM. Fig. S3c One of the half cell was heated by a block heater (NISSIN, NDC-100), and the other cell was cooled by ice (1±0.5 °C). Fig. S3d Colour of the heated cell (82 °C) turned yellow because all triiodide ions are released from starch. The yellow colour turned from back to blue immediately after the cell temperature decreased. Sample: the same as that in Fig. S3b.

# S1.8 Comparison of the results of TEC measurements with H-shape cell and Mini-cell

The results obtained by H-shape cell and Mini-cell were compared (Fig. S4). All plots were well aligned in the same line, and the results are consistent. It also infers that the size of the cell does not influence Seebeck coefficient. The estimated  $S_e$  value was 0.66 mV K<sup>-1</sup>.





# **S2.** Supplementary Results and Discussions



Figure S5. Dependence of the absorbance of triiodide (353 nm) on the concentration of  $I_2$  at varied  $[KI]_0/[I_2]_0$  ratio. The absorbance becomes linear at higher relative concentration  $[KI]/[I_2] > 100$ . Absorption coefficient of triiodide =  $2.6 \times 10^4 M^{-1} cm^{-1}$  at  $KI/I_2 = 200$ .



**Figure S6.** Variable-temperature cyclic voltammograms of samples with (a, b and c) or without (d, e and f) starch. Sample conditions of a), b) and c):  $[KI]_0 = 12.5 \text{ mM}$ ,  $[I_{2}]_0 = 2.5 \text{ mM}$ , [starch] = 60 mM, [KCI] = 200 mM. Sample conditions of d), e), f):  $[KI]_0 = 12.5 \text{ mM}$ ,  $[I_2]_0 = 2.5 \text{ mM}$ , [KCI] = 200 mM. Each plots contains voltammograms at the scan rate from 0.01 to 0.2 V s<sup>-1</sup>.



Figure S7. Cyclic voltammogram of iodide/triiodide system with different supporting electrolyte. KI: [KI] = 100 mM, [I<sub>2</sub>] = 2.5 mM, KNO<sub>3</sub>: [KI] = 12.5 mM, [I<sub>2</sub>] = 2.5 mM, [I<sub>2</sub>] = 2.5 mM, [KO<sub>3</sub>] = 0.1 M, KCI: [KI] = 12.5 mM, [I<sub>2</sub>] = 2.5 mM, [KCI] = 0.2 M, Redox reaction at peak (i)-(iv) is summarized as follows: (i)<sup>11</sup>  $3I^- \rightleftharpoons I_3^- + 2e^-$ ; (ii)<sup>11</sup>  $2I_3^- \rightleftharpoons 3I_2 + e^-$ ; (iii)<sup>12</sup>  $I^- + 2CI^- \rightleftharpoons [ICI_2]^-$ ; (iv)<sup>13</sup>  $I_2 + 2H_2O \rightleftharpoons 2HOI + 2H^+ + e^-$ .





**Figure S8.** Variable-temperature cyclic voltammograms of samples without (a-c) or with (d-i) PVP (M.W. 40k). Sample conditions of (a), (b), (c):  $[KI]_0 = 12.5 \text{ mM}$ ,  $[I_2]_0 = 2.5 \text{ mM}$ ,  $[KNO_3] = 100 \text{ mM}$ , (d), (e), (f):  $[KI]_0 = 12.5 \text{ mM}$ ,  $[I_2]_0 = 2.5 \text{ mM}$ ,  $[KNO_3] = 100 \text{ mM}$ , [PVP] = 9 mM, (g), (h), (i):  $[KI]_0 = 12.5 \text{ mM}$ ,  $[I_2]_0 = 2.5 \text{ mM}$ , [PVP] = 36 mM. Scan rate: 10-200 mV/s. Temperature: 10, 20, and 40 °C.





Figure S10. Plots of  $V_{oc}$  and  $\Delta T$  of aqueous  $|T/l_3^-$  with an addition of KCI. The concentration of starch (0, 60 mM in glucose unit) and KCI (0, 0.2, 1, 2 M) are indicated in the inset. When starch is present in the solution, the slope of the fitting line (Seebeck coefficient) increases slightly after adding KCI.



Figure S11. Open-circuit voltage vs. temperature difference in the iodide/triiodide TEC with various supporting electrolyte (base: [KI] = 12.5 mM, [I<sub>2</sub>] = 2.5 mM, KCI: [KI] = 12.5 mM, [I<sub>2</sub>] = 2.5 mM, [KI] = 12.5 mM, [KI] = 12.5 mM, [I<sub>2</sub>] = 2.5 mM, [KO<sub>3</sub>] = 0.2 M). Error bars are smaller than the size of marks. The dashed line is to guide the eye.



Figure S12. a) /–V and b) P–V curves of aqueous starch–Ir/I<sub>3</sub>– solutions with various concentration of KCI. [starch] = 60 mM. Those curves were evaluated with H-cell (Fig. S1 and S2).

b)

a)

c)



**Figure S13.** a) Time course of output current (*I*) of TEC consisting of base  $|-I|_{3}$ - solutions (without starch). External voltage ( $V_{ex}$ ) values for starch (KCl = 2 M), starch (KCl = 0.2 M) and base (KCl = 2 M), were 25, 20 and 10 mV, respectively. b) The difference of temperature ( $\Delta T$ ) between the heated and cooled sides of the TECs whose output current was measured at Fig. S6a. c) UV-vis spectra of the base electrolyte solutions (without starch) in Fig. S6a before the run (black line) and after four hours of the run (red dashed line). Each solution was diluted to 10%. The absorbance of triiodide in the electrolyte decreases after a long period of heating.

# **References:**

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