Electronic Supplementary Information

Methanol-based thermoelectric conversion device with high power

Touya Aiba[1], Haruka Yamada[2], and Yutaka Moritomo[1,2,3,4]

[1] Graduate School of Pure & Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-7571, Japan
[2] School of Science & Engineering, University of Tsukuba, Tsukuba, Ibaraki 305-7571, Japan
[3] Faculty of Pure & Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-7571, Japan
[4] Tsukuba Research Center for Energy Materials Science (TREMS), University of Tsukuba, Ibaraki 305-8571, Japan

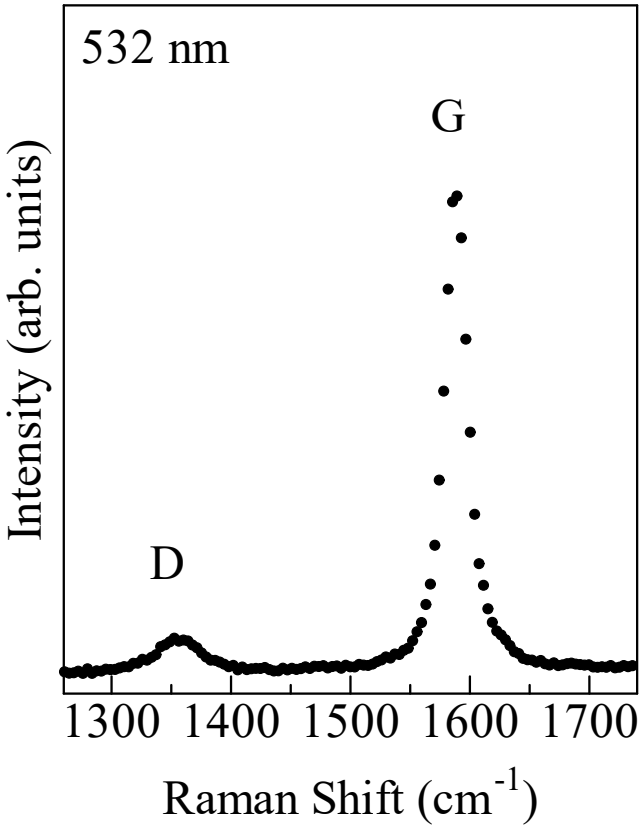

Fig. S1 Raman spectra of graphite power at room temperature. D and G represent for disorder and graphite bands, respectively. Excitation wavelength was 532 nm.

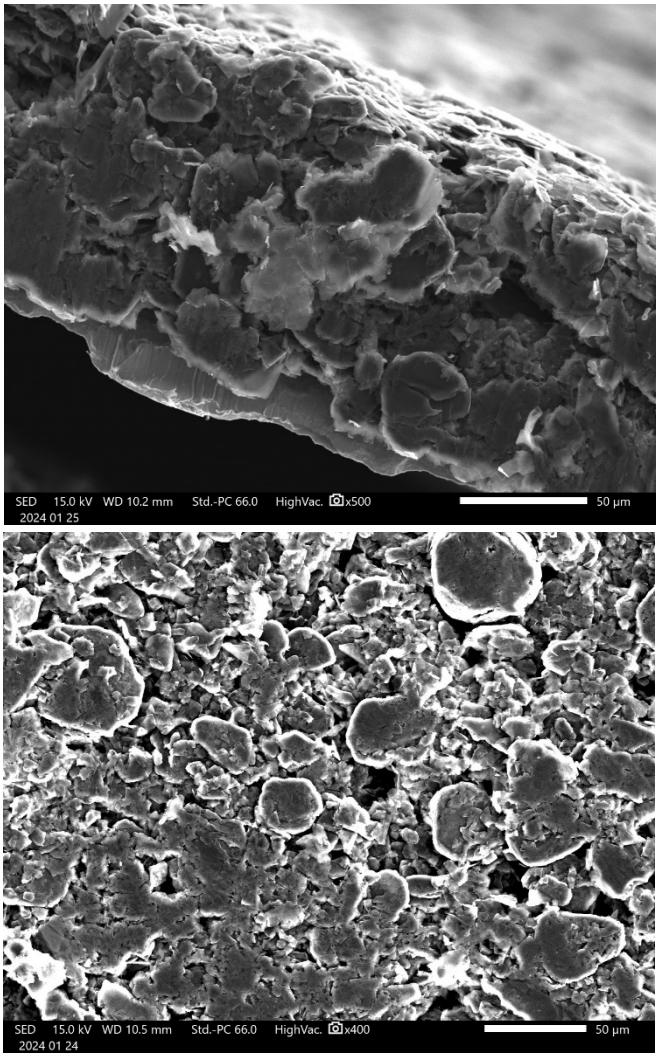

Fig. S2 Cross sectional (top) and surface (bottom) SEM images of graphite-dispersing coated electrode (t = 131 µm).

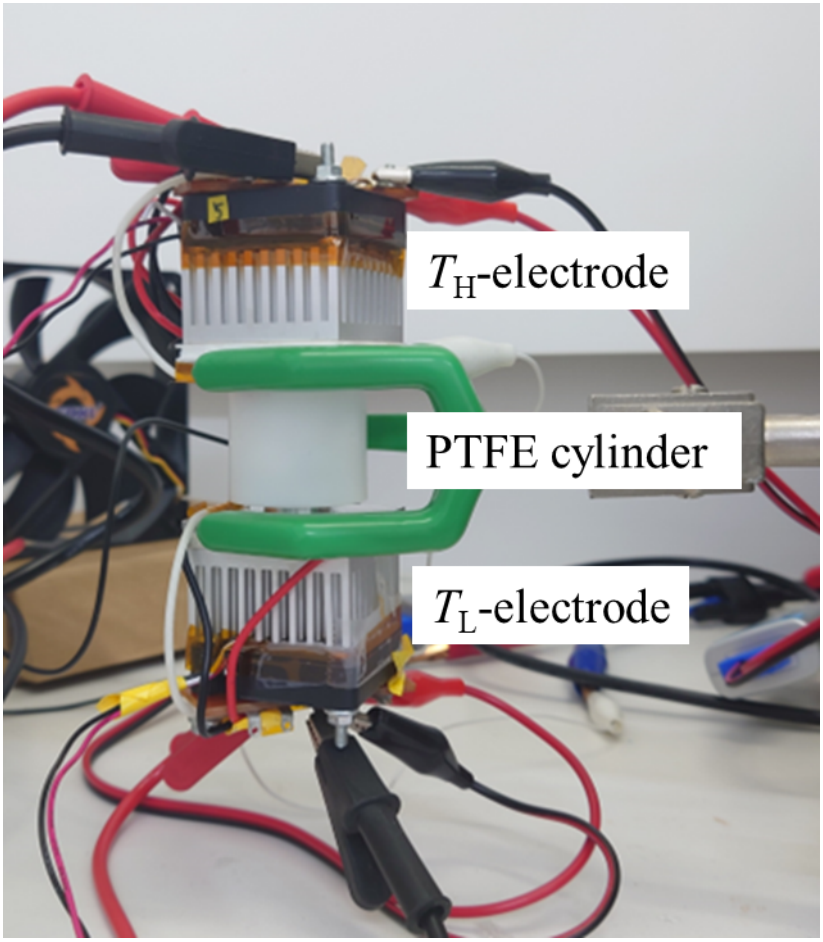

Fig.S3 Picture of LTE in the top configuration. The cell consists of a cylindrical electrolyte tank and two electrode plates. The electrolyte tank was a 7.3 mmϕ polytetrafluoroethylene (PTFE) cylinder. The electrode plate was Pt disk, whose inner surface was completely covered with the coated electrodes. An aluminum base is attached to the outside of each Pt electrode, and a Peltier element and a cooling fan are attached to the base. Temperature of the high (T_H) and low (T_L) electrodes were independently controlled with the Peltier element and cooling fan.

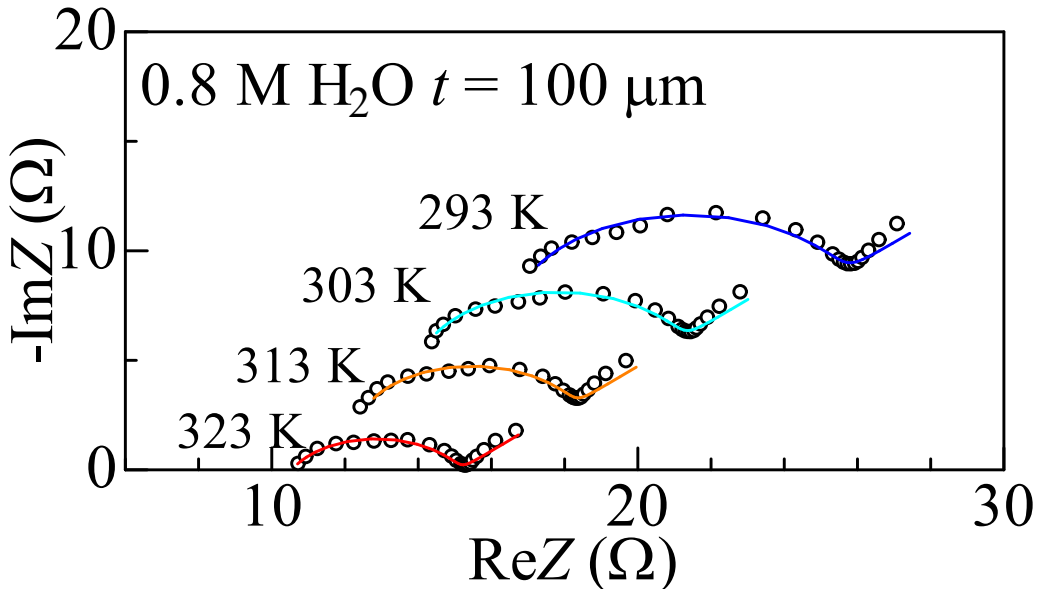

Fig. S4 Cole -- Cole plots of complex impedance in aqueous solutions containing 0.8 M $Fe(ClO_4)_2/Fe(ClO_4)_3$ at different temperature T. s and d were 42 mm^2 and 10 mm, respectively. Solid curves are the results of least-squares fits with a Randles equivalent circuit composed of R_s, R_{ct}, coherent phase element (CPE) Q, and Z_W. Q is expressed as $Q = 1/ Y_0 (i\omega)^n$, where ω is angular velocity. Y_0 and n are frequency-independent constants. n was fixed at 0.7. Q becomes pure capacitance at n = 1. The vertical axis is shifted for each plot.

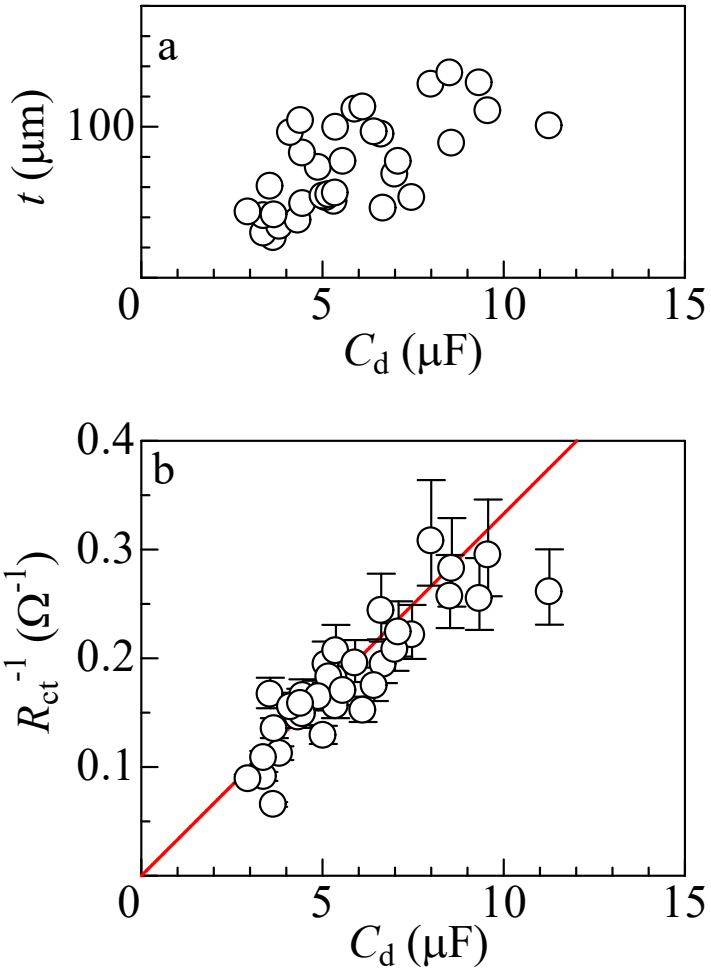

Fig. S5 Correlation between electric double layer capacitance C_d and electrode thickness t in 0.8 M $Fe(ClO_4)_2/Fe(ClO_4)_3$ MeOH solution at 298 K. (b) Correlation between C_d and reciprocal of charge-transfer resistance R_{ct}. The electrode area s and thickness t were 42 mm^2 and 10 mm, respectively. The straight line in (b) is a guide to the eye.

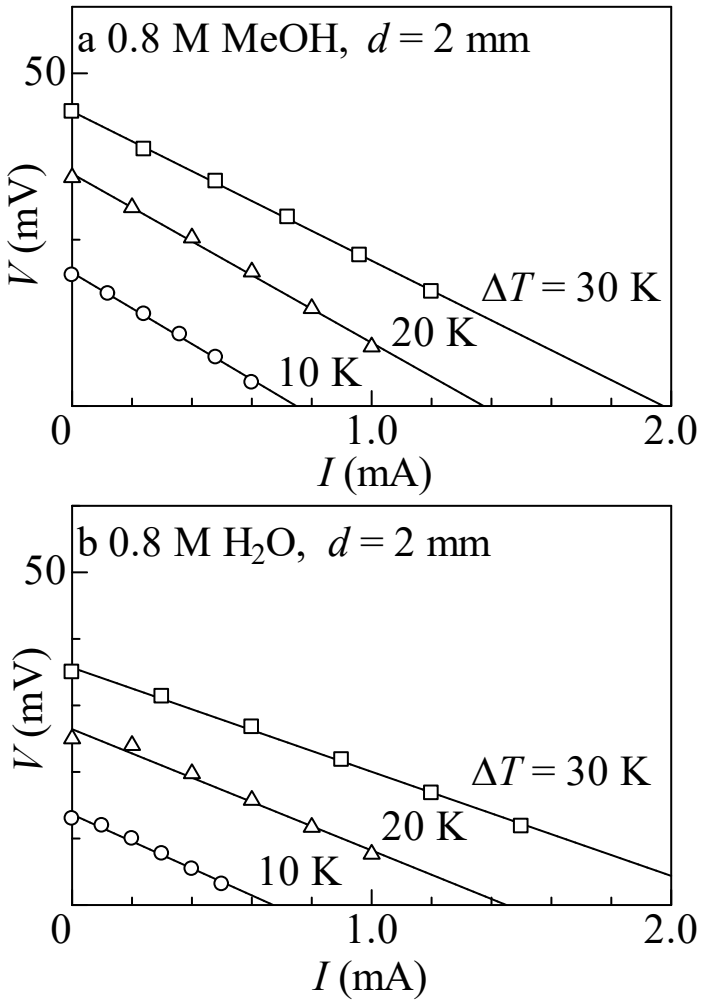

Fig. S6 I -V plot in (a) MeOH (t = 115 μm) and (b) aqueous (t = 110 μm) LTEs against ΔT in the side configuration. T_L was fixed at 298 K. s and d were 42 mm^2 and 2 mm, respectively. The electrolytes were MeOH and aqueous solutions containing 0.8 M $Fe(ClO_4)_2/Fe(ClO_4)_3$. Solid straight lines are results of least-squares fits.

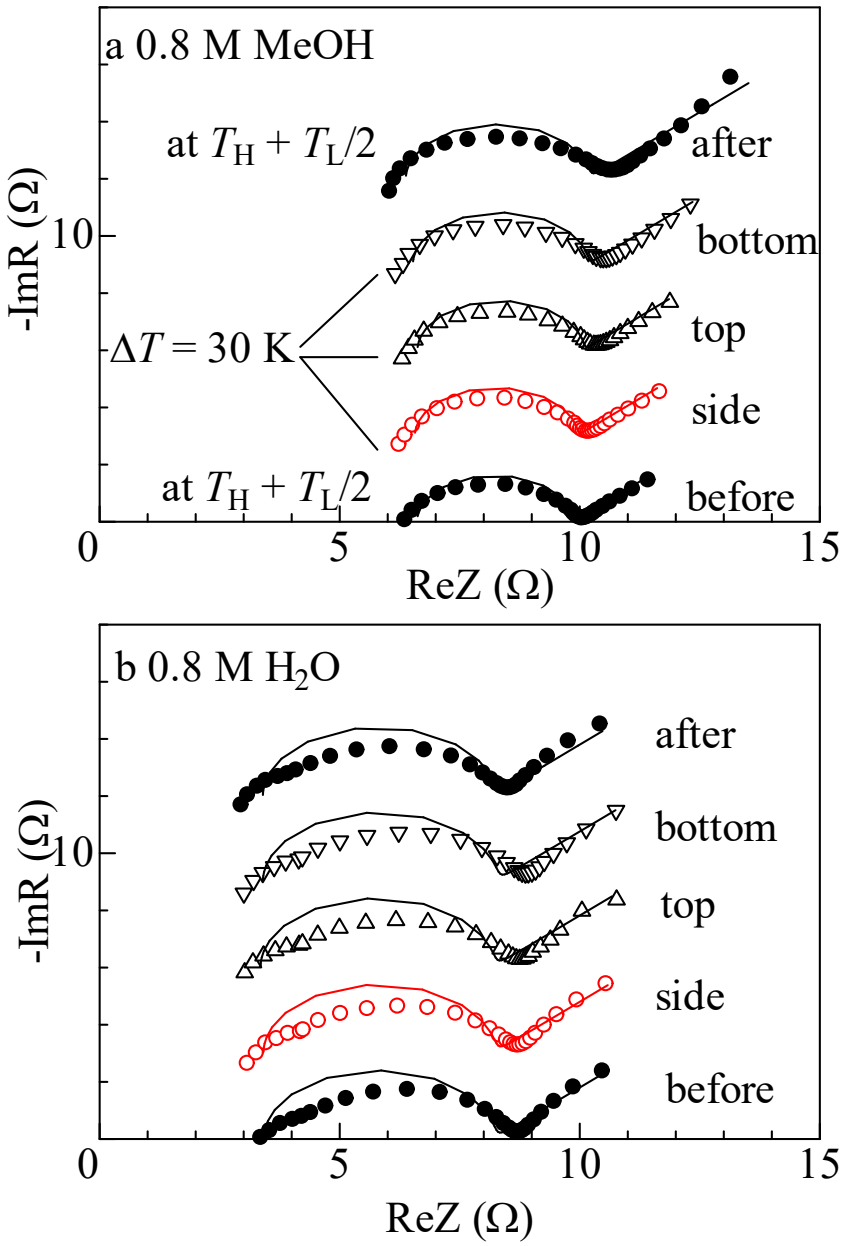

Fig. S7 Cole -- Cole plots of complex impedance in (a) MeOH and (b) aqueous LTEs at ΔT = 30 K (side, top, and bottom) and 0 K (before and after). The electrolyte was MeOH and aqueous solutions containing 0.8 M $Fe(ClO_4)_2/Fe(ClO_4)_3$. The high (T_H) and low (T_L) electrode were 293 K and 313 K, respectively. *s* and *t* were 42 mm^2 and 2 mm, respectively. Open circles triangles (inverted triangles) were measured at ΔT = 30 K in horizontally oriented LTE and vertically oriented LTE whose T_H-electrode is at the top (bottom). Filled circles were measured at T = $(T_H + T_L)/2$ K in horizontally oriented LTE before (after) the evaluation of LTE performance. Solid curves are the results of least-squares fits with a Randles equivalent circuit composed of R_s, R_{ct}, C_d, and Z_W. The vertical axis is shifted for each plot.

CPE model

Temperature (C°)	R_s (Ω)	R_{ct} (Ω)	Y_0 (μs^n/Ω)	n	A_W (Ω/s$^{1/2}$)
20	17.1(2)	8.6(3)	170(15)	0.7	0.37(3)
30	14.4(1)	6.9(2)	150(14)	0.7	0.37(3)
40	12.6(1)	5.6(2)	150(12)	0.7	0.39(3)
50	10.6(1)	4.6(2)	140(10)	0.7	0.41(3)

C_d model

Temperature (C°)	R_s (Ω)	R_{ct} (Ω)	C_d (μF)	A_W (Ω/s$^{1/2}$)
20	17.4(5)	7.8(3)	12.0(1.4)	0.30(5)
30	14.5(4)	6.5(3)	9.3(1/2)	0.34(6)
40	12.5(5)	5.4(3)	6.9(0.9)	0.35(6)
50	10.6(3)	4.5(2)	6.0(0.8)	0.40(6)

Table S1 (upper) Obtained parameters by least-squares fits with a Randles equivalent circuit composed of R_s, R_{ct}, Q, and Z_W (CPE model). Q is expressed as $Q = 1/ Y_0(i\omega)^n$, where n is fixed at 0.7. (lower) Obtained parameters by least-squares fits with a Randles equivalent circuit composed of R_s, R_{ct}, C_d, and Z_W (C_d model).

The data supporting this article

Device resistance R, solution resistance R_s, and charge-transfer resistance R_{ct} against temperature T in aqueous, MeOH, and acetone solutions containing 0.8 M $Fe(ClO_4)_2/Fe(ClO_4)_3$. s and d were 42 mm^2 and 10 mm, respectively.

#graphite wako
#0.8 M aq
#m ratio 90w%
#thickless 100 μm
#temperture[K],R_s[Ω],R_{ct}[Ω],R[Ω]

293	17.4	7.8	38.6
303	14.5	6.5	32.2
313	12.5	5.4	27.9
323	10.6	4.5	23.5

#graphite wako
#0.8 M MtOH
#m ratio 90w%
#thickless 105 μm
#temperture[K],R_s[Ω],R_{ct}[Ω]

293	57.0	3.9	78.7
303	48.9	2.8	66.6
313	42.1	2.6	56.7
323	36.8	2.6	50.6

#graphite wako
#0.8 M aceton
#m ratio 90w%
#thickless 107 μm
#temperture[K],R_s[Ω],R_{ct}[Ω],R[Ω]

293	155.0	6.3	196.0
303	130.0	5.0	167.0
313	107.0	4.3	137.0
323	84.7	2.4	111.0

R, R_s, R_{ct}, and C_d against electrode thickness t at 298 K. s and d were 42 mm^2 and 10 mm, respectively.

t[μm]	R[Ω]	R_s[Ω]	R_{ct}[Ω]	C_d[uF]
26.5	96.1	48.2	15.3	3.7
29.5	89.3	48.2	11.0	3.4
34.0	83.8	49.3	8.9	3.8
38.0	76.4	48.9	6.9	4.3
41.0	79.9	48.3	9.2	3.4
41.5	80.9	47.3	7.4	3.7
43.5	79.2	47.8	11.2	3.0
46.0	71.4	48.4	5.1	6.7
49.0	76.3	48.6	6.0	4.5
50.5	73.0	47.1	5.5 □	5.3
53.0	70.9	48.7	5.1	5.1
53.0	70.3	47.9	4.5	7.5
54.0	75.9	48.3	7.8	5.0
55.0	73.1	48.5	5.5	5.2
56.0	76.8	49.3	6.4	5.4
60.5	73.7	48.3	6.0	3.6
68.5	68.1	47.5	4.8	7.0
73.0	68.6	47.9	6.1	4.9
77.0	69.9	46.7	5.9	5.6
77.0	70.39	48.2	4.5	7.1
82.5	74.76	49.0	6.7	4.5
89.0	66.54	46.9	3.5	8.6
95.0	67.64	48.1	4.1	6.6
96.0	75.4	48.3	6.4	4.1
96.5	74.23	48.8	5.7	6.4
99.5	69.9	48.4	4.8	5.4
100.5	66.57	48.7	3.8	11.3
104.0	73.2	48.6	6.3	4.4
110.5	66.03	47.4	3.4	9.6
111.5	69.09	47.9	5.1	5.9
113.0	75.9	50.8	6.6	6.1
128.0	67.2	48.3	3.2	8.0
129.0	65.38	47.4	3.9	9.3
135.5	69.54	47.4	3.89	8.5

Voltage V against current I of MeOH (t = 115 μm) and aqueous (t = 110 μm) LTEs at ΔT = 30 K. s and d were 42 mm^2 and 2 mm, respectively. The electrolytes were MeOH and aqueous solutions containing 0.8 M $Fe(ClO_4)_2/Fe(ClO_4)_3$.

#graphite_paste 90w%
#thickless 115 μm
#side
#MeOH_0.8M
#temperture 298-328 K
I[mA], V[mV]
0.00 44.25
0.24 38.59
0.48 33.78
0.72 28.40
0.96 22.67
1.2 17.19

#graphite_paste 90w%
#thickless 115 μm
#up
#MeOH_0.8M
#temperture 298-328 K
I[mA], V[mV]
0.00 43.76
0.24 38.76
0.48 32.47
0.72 26.40
0.96 19.84
1.2 12.87

#graphite_paste 90w%
#thickless 115 μm
#down
#MeOH_0.8M
#temperture 298-328 K
I[mA], V[mV]
0.00 44.29
0.24 38.03

0.48 31.45
0.72 24.32
0.96 17.51
1.20 11.44

#graphite_paste 90w%
#thickless 110 μm
#side
#H2O_0.8M
#temperture 298-328 K
I[mA], V[mV]
0.00 36.00
0.30 32.36
0.60 27.76
0.90 22.84
1.20 17.84
1.50 12.84

#graphite_paste 90w%
#thickless 110 μm
#up
#H2O_0.8M
#temperture 298-328 K
I[mA], V[mV]
0.00 36.00
0.30 32.72
0.60 28.00
0.90 22.36
1.20 16.00
1.50 9.04

#graphite_paste 90w%
#thickless 110 μm
#down
#H2O_0.8M
#temperture 298-328 K
I[mA], V[mV]
0.00 36.00

0.30	30.90
0.60	25.56
0.90	18.54
1.20	12.40
1.50	6.14