




Cite this: *Ind. Chem. Mater.*, 2025, 3, 223

Received 9th September 2024,  
 Accepted 21st November 2024

DOI: 10.1039/d4im00113c

rs.c.li/icm

## Methanol-based thermoelectric conversion device with high power†

Touya Aiba,<sup>a</sup> Haruka Yamada<sup>b</sup> and Yutaka Moritomo  \*abcd

A liquid thermoelectric conversion device (LTE) converts environmental heat into electric power via the electrochemical Seebeck coefficient  $\alpha$ . The maximum power ( $W_{\max}$ ) is expressed as  $W_{\max} = \frac{\alpha^2 \Delta T^2}{4R'}$ , where  $\Delta T$  and  $R'$  are the temperature difference between electrodes and device resistance in operation, respectively. Here, we systematically investigated the resistance components of LTEs composed of aqueous, methanol (MeOH) and acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . We found that the charge transfer resistance  $R_{\text{ct}}$  of the MeOH LTE is the smallest among the three LTEs. We demonstrated that the  $W_{\max}$  of the MeOH LTE is slightly larger than or comparable with that of the corresponding aqueous LTE. We further discussed the effects of the convection of an electrolyte on  $R'$ .

Keywords: Liquid thermoelectric conversion; Methanol; Resistivity components; Coated electrode.

### 1 Introduction

Energy harvesting devices are extensively investigated from the viewpoint of achieving the sustainable development goals (SDGs). Among the devices, liquid thermoelectric conversion devices (LTEs)<sup>1–5</sup> have a simple device structure in which a redox-dissolved electrolyte is sandwiched between two electrodes. LTEs utilize the thermogalvanic effect (electrochemical Seebeck coefficient  $\alpha$ ) at each electrode to convert temperature differences  $\Delta T$  between the electrodes into thermal voltage or electric power  $W$ . The research of LTE is increasingly active with significant progress.<sup>6–23</sup> The performance of LTE is determined by  $\alpha$ , effective electric conductivity  $\sigma$ , and effective thermal conductivity  $\kappa$  of the electrolyte. The term “effective” is used because the convection of the electrolyte due to gravity affects  $\sigma$  and  $\kappa$  in an actual LTE in operation.<sup>24–26</sup> The maximum power ( $W_{\max}$ ) is expressed as  $W_{\max} = \frac{\alpha^2 \Delta T^2}{4R'}$ , where  $R'$  is the device

resistance in operation. To increase  $W_{\max}$ , it is effective to increase  $\alpha$  or to decrease  $R'$ .  $\alpha$  is expressed as  $\alpha = \frac{\Delta S}{e}$ , where  $\Delta S$  and  $e$  ( $>0$ ) are the entropy change at the reduction reaction of the redox couple and elementary charge.

In a non-operating LTE at  $\Delta T = 0$  K without electrolyte convection, the device resistance ( $R$ ) can be decomposed into solution resistance  $R_s$ , charge transfer resistance  $R_{\text{ct}}$ , and diffusion resistance  $R_{\text{dif}}$ .<sup>27</sup> Similar to the resistance in a solid,  $R_s$  is determined by the balance between the electric force and frictional force. Then,  $R_s$  is proportional to the electrode distance  $d$ .<sup>28</sup> On the other hand,  $R_{\text{ct}}$  and  $R_{\text{dif}}$  are governed by the redox reaction kinetics in the vicinity of the electrode, and are independent of  $d$ . As the reaction progresses, the concentration of reactants/products at the electrode surface changes in a way that prevents further reaction. The resultant concentration gradient drives the diffusion of reactants from (products into) the bulk region, causing  $R_{\text{dif}}$ . In a LTE in operation,  $R'$  is further influenced by the electrolyte convection driven by  $\Delta T$ ,<sup>25,26</sup> which causes mass transfer and tends to make the concentration in the electrolyte uniform.

Aqueous solutions containing  $\text{Fe}^{2+}/\text{Fe}^{3+}$  are most extensively investigated as electrolytes for LTE, because  $\text{Fe}^{2+}/\text{Fe}^{3+}$  is inexpensive and aqueous LTE shows high  $\sigma$ . Kim *et al.*<sup>20</sup> reported that  $\alpha$  and  $\sigma$  of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  aqueous solutions become larger when  $\text{ClO}_4^-$  is the counter anion. Buckingham *et al.*<sup>21</sup> demonstrated that  $\alpha$  of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  aqueous solutions can be optimized by the pH of the electrolyte. Jung *et al.*<sup>22</sup> reported that FeCN coated carbon cloth shows small  $R_{\text{ct}}$  in  $\text{Fe}^{2+}/\text{Fe}^{3+}$  aqueous solution. Aiba *et al.*<sup>28</sup> reported that  $R$  of graphite-dispersing coated electrodes steeply decreases as the

<sup>a</sup> Graduate School of Pure & Applied Science, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan. E-mail: moritomo.yutaka.gf@u.tsukuba.ac.jp

<sup>b</sup> School of Science & Engineering, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

<sup>c</sup> Faculty of Pure & Applied Science, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

<sup>d</sup> Tsukuba Research Center for Energy Materials Science (TREMS), University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

† Electronic supplementary information (ESI) available: Raman scattering spectrum of graphite powder, SEM images of the coated electrode, picture of LTE, Cole-Cole plots analyzed with a CPE model, correlation between  $C_d$  and  $t$  ( $C_d$  and  $R_{\text{ct}}^{-1}$ ),  $I$ - $V$  plots of LTE against  $\Delta T$ , and Cole-Cole plots of LTE against  $\Delta T$  and orientation. See DOI: <https://doi.org/10.1039/d4im00113c>



electrode thickness  $t$  increases below  $t \leq 100 \mu\text{m}$ . On the other hand, Wake *et al.*,<sup>18,19</sup> systematically investigated  $\alpha$  and  $\sigma$  of organic solutions containing  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . They found that the  $\sigma$  ( $= 34.6 \text{ mS cm}^{-1}$  at 0.7 M) of methanol (MeOH) solution is the highest among those of 11 organic solutions. In addition, the  $\alpha$  values of MeOH ( $1.85 \text{ mV K}^{-1}$  at 0.5 M) and acetone ( $2.88 \text{ mV K}^{-1}$  at 0.1 M) are much higher than the  $\alpha$  ( $= 1.56 \text{ mV K}^{-1}$  at 0.5 M) of aqueous solution. Therefore, MeOH and acetone LTEs are alternative LTE candidates with high  $W_{\text{max}}$ .

In this paper, we systematically investigated the resistance components of LTEs composed of aqueous, MeOH and acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . We found that the  $R_{\text{ct}}$  of the MeOH LTE is the smallest among the three LTEs. We demonstrated that the  $W_{\text{max}}$  of the MeOH LTE is slightly larger than or comparable with that of the corresponding aqueous LTE. We further discussed the effects of the electrolyte convection on  $R'$ .

## 2 Results and discussion

### 2.1 Resistance components against temperature

Fig. 1a shows the current  $I$ -voltage  $V$  plots at  $\Delta T = 0 \text{ K}$  in (a) aqueous, (b) MeOH, and (c) acetone solutions containing 0.8

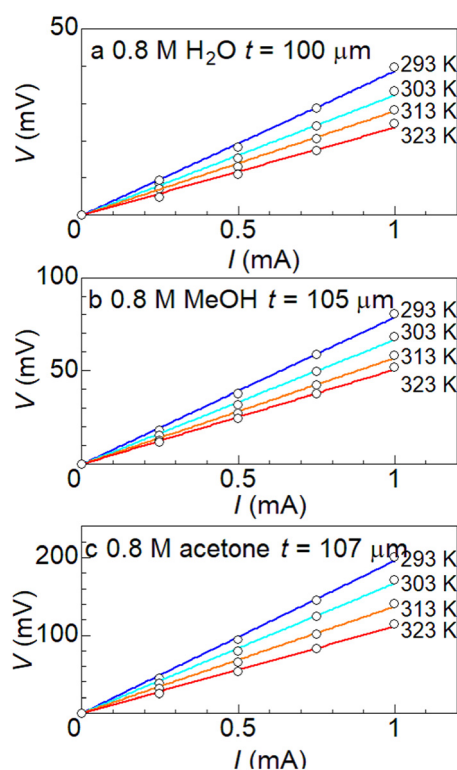


Fig. 1 Voltage  $V$  against current  $I$  in (a) aqueous, (b) MeOH, and (c) acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  at different temperatures  $T$ . The electrode area  $s$  and distance  $d$  were  $42 \text{ mm}^2$  and  $10 \text{ mm}$ , respectively. The straight lines are the results of least-squares fits.

M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  at different temperatures  $T$ .  $s$  and  $d$  were  $42 \text{ mm}^2$  and  $10 \text{ mm}$ , respectively. At all temperatures,  $V$  increases in proportion to  $I$ .  $R$  was evaluated from the slope of the plot, as indicated by straight lines.  $R$  steeply decreases as  $T$  increases.

Fig. 2 shows the Cole-Cole plots of complex impedance in (a) aqueous, (b) MeOH, and (c) acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  at different  $T$ .  $s$  and  $d$  were  $42 \text{ mm}^2$  and  $10 \text{ mm}$ , respectively. The Cole-Cole plot in (a) aqueous solution at 293 K shows a prototypical shape. The plot shows a semicircle at the left side and a straight line with an inclination of 45 degrees at the right side. The resistances at the left and right sides of the semicircle correspond to  $R_s$  and  $R_s + R_{\text{ct}}$ , respectively. Solid curves are the results of least-squares fits with a Randles equivalent circuit composed of  $R_s$ ,  $R_{\text{ct}}$ , electric double layer capacitance  $C_d$ , and Warburg impedance  $Z_W$ .  $Z_W$  is expressed as  $Z_W = A_W(\omega^{-1/2} - i\omega^{-1/2})$ , where  $A_W$  is the Warburg coefficient. The feature of the observed impedance is reproduced by the Randles equivalent circuit model. Similar behaviors are also observed at difference  $T$  and in different solutions. One may notice that the observed semicircle in (a) aqueous solution is slightly flattened as compared with the calculated one. The deviation between them can be improved if we replace  $C_d$  with constant phase element (CPE)  $Q$ , as shown in Fig. S4.†  $Q$  is

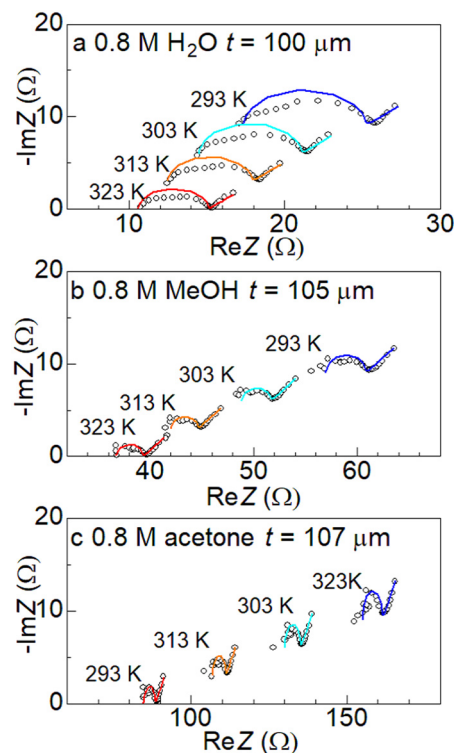


Fig. 2 Cole-Cole plots of complex impedance in (a) aqueous, (b) MeOH, and (c) acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  at different temperatures  $T$ .  $s$  and  $d$  were  $42 \text{ mm}^2$  and  $10 \text{ mm}$ , respectively. Solid curves are the results of least-squares fits with a Randles equivalent circuit composed of  $R_s$ ,  $R_{\text{ct}}$ ,  $C_d$ , and  $Z_W$ . The vertical axis is shifted for each plot.



expressed as  $Q = \frac{1}{Y_0(i\omega)^n}$  where  $\omega$  is the angular velocity.  $Y_0$  and  $n$  are frequency-independent constants.  $Q$  becomes pure capacitance at  $n = 1$ . We note that there is little change in  $R_s$  and  $R_{ct}$  between the  $C_d$  and CPE models (Table S1†).

Fig. 3 shows  $R$  (filled circles),  $R_s$  (open squares), and  $R_{ct}$  (open circles) against  $\frac{1}{T}$  in (a) aqueous, (b) MeOH, and (c) acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . In (a) aqueous solution,  $R$ ,  $R_s$ , and  $R_{ct}$  increase as  $\frac{1}{T}$  increases. We evaluated the activation energy  $\Delta_i$  ( $i = s$  and  $ct$ ) by least-squares fits with activation-type functions,  $R_i \propto e^{\frac{\Delta_i}{RT}}$  [solid curves in Fig. 3a]. The activation energies are determined as  $\Delta_s = 1550$  K and  $\Delta_{ct} = 1730$  K. Similar behaviors are observed in (b) MeOH and (c) acetone solutions even though  $R_{ct}$  is scattered at higher temperatures. In (b) MeOH solution, the activation energies are  $\Delta_s = 1380$  K and  $\Delta_{ct} = 1360$  K. In (c) acetone solution, the activation energies are  $\Delta_s = 1830$  K and  $\Delta_{ct} = 2420$  K.

Here, let's consider the solution dependence of the resistance components. The magnitudes of  $R$  and  $R_s$  gradually increase in the order aqueous, MeOH, and acetone solutions. We note that  $R_{ct}$  in MeOH solution is the smallest among the three solutions.

Here, we recall that the magnitude of  $R_s$  is proportional to  $d$  (ref. 28) and can be reduced by reducing  $d$ . Then, it may be possible to make the  $R$  of the MeOH LTE comparable to or smaller than that of the aqueous LTE. Thus, the MeOH LTE with small  $d$  is a promising LTE candidate with high  $W_{\text{max}}$ .

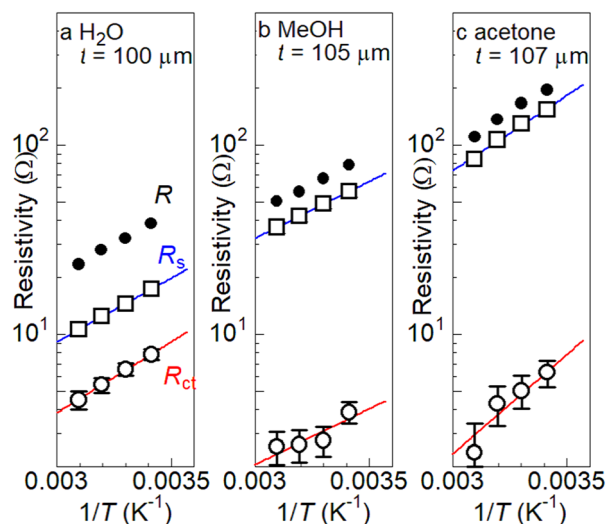


Fig. 3 Device resistance  $R$  (filled circles), solution resistance  $R_s$  (open squares), and charge-transfer resistance  $R_{ct}$  (open circles) against the reciprocal of temperature  $T$  in (a) aqueous, (b) MeOH, and (c) acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ .  $s$  and  $d$  were  $42 \text{ mm}^2$  and  $10 \text{ mm}$ , respectively. The solid curves are the results of least-squares fits with activation-type functions,  $R_i \propto e^{\frac{\Delta_i}{RT}}$  ( $i = s$  and  $ct$ ), where  $\Delta_i$  is the activation energy.

## 2.2 Scaling relation between $R_s$ and viscosity $\eta$

Now, let us discuss the solution parameter that governs the magnitude of  $R_s$ . In bulk solution, the  $j$ -th ion feels both the electric force ( $= |z_j|eE$ , where  $|z_j|$ ,  $e$ , and  $E$  are the charge number of the  $j$ -th ion, elementary charge, and electric field, respectively) and frictional force proportional to the velocity  $v_j$  of the  $j$ -th ion. According to Stokes' law, the frictional force is given as  $6\pi\eta r_j v_j$ , where  $\eta$  and  $r_j$  are the viscosity of the solution and effective radius of the  $j$ -th ion, respectively.

Then, the mobility ( $u_j \equiv \frac{v_j}{E}$ ) of the  $j$ -th ion is given as

$$u_j = \frac{|z_j|e}{6\pi\eta r_j}$$

On the other hand,  $R_s^{-1}$  is expressed as  $R_s^{-1} = \frac{sF}{d} \sum_j |z_j| u_j c_j$ ,<sup>27</sup> where  $F$  and  $c_j$  are the Faraday constant and molar concentration of the  $j$ -th ion, respectively.

By substituting  $u_j = \frac{|z_j|e}{6\pi\eta r_j}$ , we obtain  $R_s^{-1} = \frac{sFe}{6\pi d\eta} \sum_j \frac{c_j |z_j|^2}{r_j}$ .

Note that  $c_j$  and  $z_j$  are fixed in the present investigation. If the solution dependence of  $r_j$  can be ignored,  $R_s$  is proportional to  $\eta$ .

Fig. 4(a) shows  $\eta$  against  $T$  in aqueous (open squares), MeOH (open circles), and acetone (open triangles) solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . The  $T$ -dependence of  $\eta$  was evaluated using a sine-wave vibro viscometer (SV-10; A&D Company Limited) equipped with a heat bath. In all solutions,  $\eta$  steeply decreases with  $T$ . Fig. 4b shows the correlation between  $\eta$  and  $R_s$ . Open squares, circles, and triangles represent the  $\eta$  of aqueous, MeOH and acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ , respectively.  $s$  and  $d$  were  $42 \text{ mm}^2$  and  $10 \text{ mm}$ , respectively. The straight line in (b) is the result of least-squares fits.

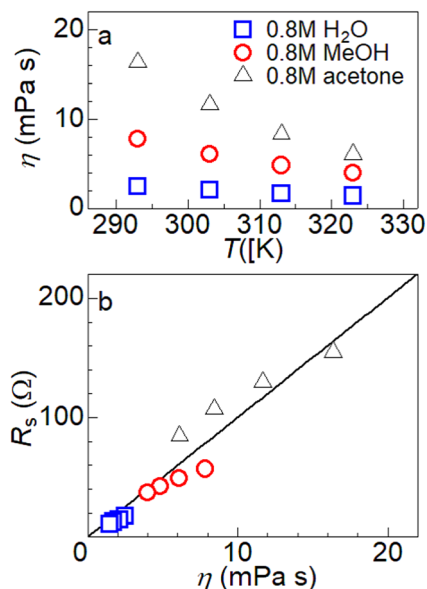


Fig. 4 (a) Viscosity  $\eta$  against temperature  $T$  in aqueous (open squares), MeOH (open circles), and acetone (open triangles) solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ ; (b) correlation between  $\eta$  and  $R_s$ . Open squares, circles, and triangles represent the  $\eta$  of aqueous, MeOH and acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ , respectively.  $s$  and  $d$  were  $42 \text{ mm}^2$  and  $10 \text{ mm}$ , respectively. The straight line in (b) is the result of least-squares fits.



triangles represent the  $\eta$  of aqueous, MeOH and acetone solutions containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ , respectively. As shown by the straight line,  $R_s$  increases almost linearly with  $\eta$  regardless of the solvent type. This observation indicates that the magnitude of  $R_s$  is governed by the  $\eta$  of the solution. In other words, the development of low- $\eta$  solution would lead to a reduction in  $R_s$ . We note that the scaling relationship between  $\eta$  and  $R_s$  does not hold in the dilute solution. The  $\eta$  of the solvent increases in the order acetone (0.32 mPa s), MeOH (0.62 mPa s) and water (1.01 mPa s). Nevertheless,  $R$  is the smallest in aqueous solution even at 0.1 M.<sup>18</sup>

### 2.3 Resistance components of MeOH solution against $t$

Fig. 4a shows the  $I$ - $V$  plots at different  $t$  in 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  MeOH solution at 298 K.  $s$  and  $d$  were 42 mm<sup>2</sup> and 10 mm, respectively. For all electrodes,  $V$  increases in proportion to  $I$ .  $R$  was evaluated from the slope of the plot. Importantly,  $R$  decreases as  $t$  increases. Fig. 4b shows the Cole-Cole plots of complex impedance at different  $t$  in 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  MeOH solution at 298 K.  $s$  and  $d$  were 42 mm<sup>2</sup> and 10 mm, respectively. 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 observed impedance is well reproduced by the Randles equivalent circuit model.

Fig. 6a shows  $R^{-1}$  against  $t$ .  $R^{-1}$  slightly increases as  $t$  increases in the small  $t$  region ( $t \leq 60 \mu\text{m}$ ), and then is saturated to about 0.014  $\Omega^{-1}$ . Fig. 5b shows  $R_s^{-1}$  against  $t$ .  $R_s^{-1}$  ( $= 0.021 \Omega^{-1}$ ) is almost independent of  $d$ , because the macroscopic electric force between the electrodes is

independent of the electrode structure. A similar  $t$ -independent behavior of  $R_s$  is observed in 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  aqueous solution.<sup>28</sup>

Fig. 6c shows  $R_{ct}^{-1}$  against  $t$ . In the small  $t$  region ( $t \leq 50 \mu\text{m}$ ),  $R_{ct}^{-1}$  increases as  $t$  increases. In the large  $t$  region ( $t \geq 50 \mu\text{m}$ ), however,  $R_{ct}^{-1}$  is seriously scattered. This is probably because the degree of dispersion of the graphite particles varies from electrode to electrode, causing the scattering if the data were plotted against  $t$ . On the other hand,  $R_{ct}^{-1}$  is expected to increase in proportion to the electrochemically active surface area (EASA), which is usually evaluated by the  $C_d$  of the electrode.<sup>29-31</sup> We investigated a correlation between  $C_d$  and  $t$  [Fig. S5a†] and correlation between  $C_d$  and  $R_{ct}^{-1}$  [Fig. S5b†]. We found that the correlation between  $C_d$  and  $t$  is poor, supporting our idea that the degree of dispersion varies from electrode to electrode. Nevertheless, we found a good correlation between  $C_d$  and  $R_{ct}^{-1}$ , indicating that  $R_{ct}^{-1}$  is proportional to the EASA.

### 2.4 Output characteristics of MeOH LTE

First, let us investigate the effect of the LTE orientation on output power  $W$ . Fig. 7a shows the output characteristics of MeOH whose  $d$  is 2 mm. The high ( $T_H$ ) and low ( $T_L$ ) electrodes were 298 K and 328 K, respectively.  $\Delta T$  was fixed at 30 K. The electrolyte is MeOH solution containing 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . The circles were the data of horizontally oriented LTEs (denoted as “side”). The triangles and inverted triangles were the data of vertically oriented LTEs whose  $T_H$ -

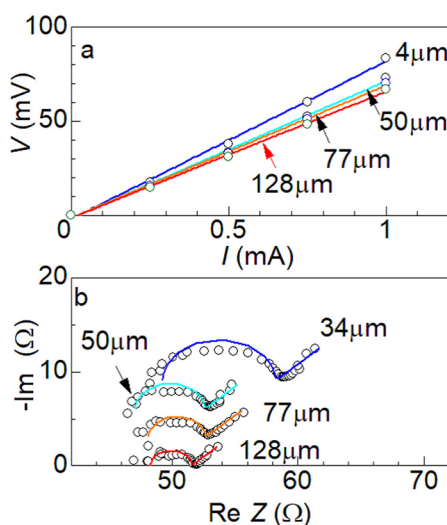


Fig. 5 (a) Voltage  $V$  against current  $I$  in 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  MeOH solution at 298 K at different electrode thicknesses  $t$ ; (b) Cole-Cole plots of complex impedance in 0.8 M  $\text{Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$  MeOH solution at 298 K at different  $t$ .  $s$  and  $d$  were 42 mm<sup>2</sup> and 10 mm, respectively. Straight lines in (a) are the results of least-squares fits. Solid curves in (b) 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 in (b) is shifted for each plot.

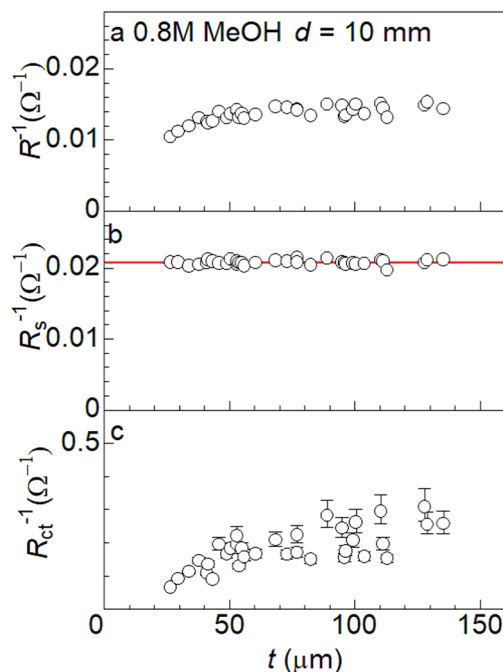
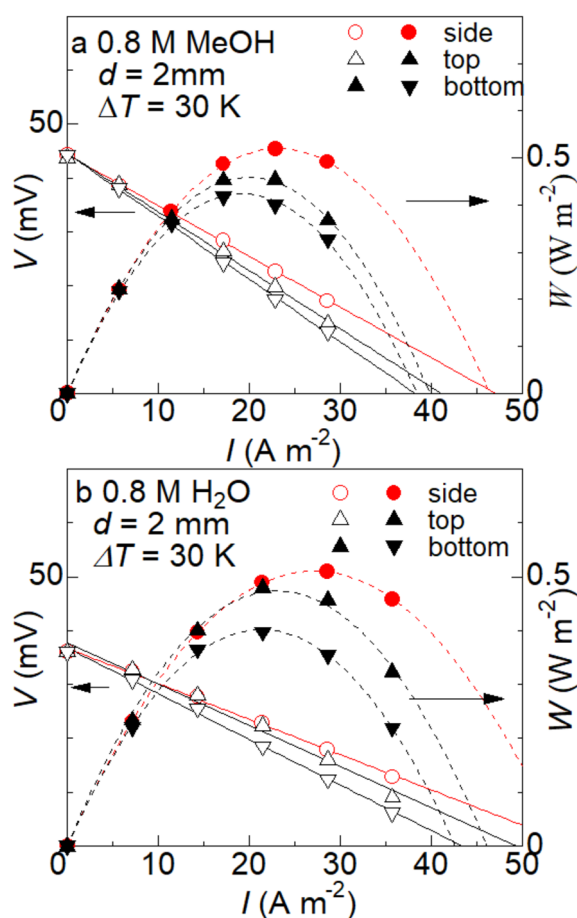


Fig. 6 Reciprocal of (a)  $R$ , (b)  $R_s$ , and (c)  $R_{ct}$  against electrode thickness  $t$  at 298 K.  $s$  and  $d$  were 42 mm<sup>2</sup> and 10 mm, respectively. The solid red straight line in (b) is the result of least-squares fits.



electrode is at the top and bottom, respectively. In both the LTEs,  $\alpha \left( = \frac{V_0}{\Delta T} \right)$  does not show any orientation dependence. The  $\alpha$  values of the MeOH (aqueous) LTE are 1.48 (1.22), 1.48 (1.25), and 1.48 (1.22) mV K<sup>-1</sup> in the side, top, and bottom configurations, respectively. This is because  $\alpha$  is governed by the entropy change at the reduction reaction and is not affected by the electrolyte convection. On the other hand,  $W$  shows significant orientation dependence. We evaluated the  $V_0$  and  $R'$  of the LTE in operation by least-squares fit of the  $I$ - $V$  plot.  $W_{\max} \left( = \frac{V_0^2}{4R'} \right)$  steeply decreases in the order side (0.52 W m<sup>-2</sup>), top (0.45 W m<sup>-2</sup>), and bottom (0.42 W m<sup>-2</sup>) configurations. A similar orientation effect is also observed in the aqueous LTE whose  $d$  is 2 mm (Fig. 7b).  $W_{\max}$  steeply decreases in the order side (0.51 W m<sup>-2</sup>), top (0.46 W m<sup>-2</sup>), and bottom (0.40 W m<sup>-2</sup>) configurations.

The observed orientation effect can be ascribed to the convection of the electrolyte caused by gravity. Yang *et al.*<sup>25</sup>



**Fig. 7** Output voltage  $V$  and power density  $W$  against current density  $I$  of (a) MeOH ( $t = 115 \mu\text{m}$ ) and (b) aqueous ( $t = 110 \mu\text{m}$ ) LTEs at  $\Delta T = 30 \text{ K}$ .  $s$  and  $d$  were  $42 \text{ mm}^2$  and  $2 \text{ mm}$ , respectively. The electrolytes were MeOH and aqueous solutions containing  $0.8 \text{ M Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . The circles are the data of horizontally oriented LTEs. The triangles and inverted triangles are the data of vertically oriented LTEs whose  $T_{\text{H}}$ -electrode is at the top and bottom, respectively. Solid straight lines are the results of least-squares fits of the  $I$ - $V$  plots. Broken curves are the results of least-squares fits with quadratic function.

investigated the convection effect on  $W$  through fluid simulations. In a horizontally oriented LTE, the direction of temperature difference is perpendicular to that of gravity. Then, the electrolyte near the  $T_{\text{H}}$ -electrode rises, and then moves to the  $T_{\text{L}}$ -electrode when it reaches the top of the electrode. The electrolyte near the  $T_{\text{L}}$ -electrode descends, and moves to the  $T_{\text{H}}$ -electrode when it reaches the bottom of the electrode. The resultant uniform convection throughout the electrolyte effectively carries consumed redox ions to the respective electrode and promotes the redox reaction there. In a vertically oriented LTE, the direction of temperature difference is parallel to that of gravity, and hence, uniform convection throughout the electrolyte is difficult. Then, the redox reaction at the electrode is not promoted as much, because consumed ions are not sufficiently supplied by the electrolyte convection. Consistent with our observation, their simulation<sup>25</sup> showed that  $W$  decreases in the order side, top, and bottom configurations.

Next, let us compare the  $W_{\max}$  of (a) MeOH LTE with that of (b) aqueous LTE. In the side configuration, the  $W_{\max}$  ( $= 0.52 \text{ W m}^{-2}$ ) of the MeOH LTE is comparable with the  $W_{\max}$  ( $= 0.51 \text{ W m}^{-2}$ ) of the corresponding aqueous LTE. In the top configuration, the  $W_{\max}$  ( $= 0.45 \text{ W m}^{-2}$ ) of the MeOH LTE is comparable with the  $W_{\max}$  ( $= 0.46 \text{ W m}^{-2}$ ) of the corresponding aqueous LTE. In the bottom configuration, the  $W_{\max}$  ( $= 0.42 \text{ W m}^{-2}$ ) of the MeOH LTE is 5% larger than the  $W_{\max}$  ( $= 0.40 \text{ W m}^{-2}$ ) of the corresponding aqueous LTE. Thus, we demonstrated that the  $W_{\max}$  of the MeOH LTE is slightly larger than or comparable with that of the corresponding aqueous LTE. The large  $W_{\max}$  of the MeOH LTE is ascribed to the large  $\alpha$  and small  $R_{\text{ct}}$ , because the former causes high  $V_0$  and the latter causes small  $R'$ . In Table 1, we compare the obtained  $W_{\max}$  of the MeOH LTE with those of aqueous LTEs containing  $\text{Fe}^{2+}/\text{Fe}^{3+}$  reported in the literature. We note that the effective electric conductivity  $\sigma$  strongly depends on  $d$  and  $\Delta T$ , reflecting that  $R_{\text{ct}}$  and  $R_{\text{dif}}$  are independent of  $d$  and the convection effect is driven by  $\Delta T$ . Therefore, a direct comparison of  $W_{\max}$  evaluated at different  $d$  and  $\Delta T$  is difficult. Roughly speaking, however, the  $W_{\max}$  of the MeOH LTE is comparable with those of aqueous LTEs reported so far.

The dimensionless figure of merit  $\left( ZT = \frac{\alpha \sigma^2 T}{\kappa} \right)$  is a significant parameter of LTE, since  $ZT$  determines the thermal efficiency  $\eta$ . Nishitani *et al.*<sup>32</sup> reported the  $\kappa$  of several solutions containing  $\text{Fe}_2(\text{ClO}_4)_2/\text{Fe}_3(\text{ClO}_4)_3$ . The  $\kappa$

**Table 1** Output characteristics of LTEs containing  $\text{Fe}^{2+}/\text{Fe}^{3+}$ .  $\Delta T$ ,  $d$ ,  $s$ , and  $W_{\max}$  are the temperature difference, electrode distance, electrode area, and maximum output, respectively

Solvent	$\Delta T$ (K)	$d$ (mm)	$s$ (mm <sup>2</sup> )	$W_{\max}$ (W m <sup>-2</sup> )	Ref.
H <sub>2</sub> O	25	8	64	0.60	20
H <sub>2</sub> O	20	7	200	0.07	21
H <sub>2</sub> O	30	10	13	0.50	22
H <sub>2</sub> O	30	2	42	0.51	This work
MeOH	30	2	42	0.52	This work



**Table 2** Device resistance ( $R'$ ) of LTEs in operation ( $\Delta T = 30$  K) together with the device resistance ( $R$ ) of the non-operating LTE ( $\Delta T = 0$  K).  $s$  and  $d$  were  $42 \text{ mm}^2$  and  $2 \text{ mm}$ , respectively. The electrolytes were MeOH and aqueous solutions containing  $0.8 \text{ M Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . The high ( $T_H$ ) and low ( $T_L$ ) electrodes were  $298 \text{ K}$  and  $328 \text{ K}$ , respectively.  $R$  was measured at  $T_L$  and  $T_H$ . Side means that the LTE was oriented horizontally. Top and bottom means that the LTE was oriented vertically with the  $T_H$ -electrode located at the top and bottom, respectively

	$R' (\Omega)$			$R (\Omega)$	
	Side	Top	Bottom	$T_L$	$T_H$
MeOH	22.4	25.9	27.7	27.3	20.8
H <sub>2</sub> O	17.0	18.2	20.2	18.6	13.5

values at  $0.8 \text{ M}$  are  $0.23$  and  $0.46 \text{ W m}^{-1} \text{ K}^{-1}$  in the MeOH and aqueous solutions.  $\alpha \left( = \frac{V_0}{\Delta T} \right)$  of the MeOH and aqueous LTEs can be evaluated from Fig. 7:  $\alpha = 1.48$  and  $1.22 \text{ mV K}^{-1}$ , respectively.  $\sigma \left( = \frac{d}{sR'} \right)$  of the MeOH and aqueous LTEs can be evaluated from Table 2:  $\sigma = 0.213$  and  $0.280 \text{ S cm}^{-1}$  in the side configuration. We obtained  $ZT = 0.040$  and  $0.018$  in the MeOH and aqueous LTEs, respectively. The larger  $ZT$  in the MeOH LTE is ascribed to the smaller  $\kappa$  of MeOH solution.

### 2.5 Resistance components of LTE in operation

Table 2 shows the  $R'$  of the operating LTEs ( $\Delta T = 30 \text{ K}$ ) and the  $R$  of the non-operating LTE. We carefully performed a series of measurements using the same LTE. Looking at Table 2, one may notice a significant orientation dependence of  $R'$ ;  $R'$  decreases in the order side, top, and bottom configurations. As discussed in the previous subsection, the orientation effect can be ascribed to the electrolyte convection driven by  $\Delta T$ . We further investigated the  $\Delta T$  dependence of  $R'$  in the side configuration with fixing  $T_L$  at  $298 \text{ K}$  (Fig. S6†). In the MeOH and aqueous LTEs,  $R'$  decreases as  $\Delta T$  increases:  $R' = 26.8$  (20.3),  $24.4$  (18.2), and  $22.4$  (15.6);  $\Omega$  at  $\Delta T = 10, 20$  and  $30 \text{ K}$ , respectively. It is reasonable that the convection effect becomes stronger ( $R'$  becomes smaller) as  $\Delta T$  increases. We further performed EIS measurements of the operating and non-operating LTEs. The Cole–Cole plot of the operating LTE is almost the same as that of the non-operating LTE at  $T = \frac{T_H + T_L}{2}$  (Fig. S7†). In the MeOH and aqueous LTEs,  $R_s = 6.4$ – $6.6$  (3.4)  $\Omega$  and  $R_{ct} = 3.2$ – $3.5$  (4.8)  $\Omega$ , respectively. Therefore, the convection effect in the operating LTE mainly affects  $R_{dif}$ , but has little effect on  $R_s$  and  $R_{ct}$ .

Finally, let us compare  $R'$  with the average value of  $R$  at  $T_L$  and  $T_H$ . In the MeOH LTE,  $R'$  in the top and bottom configurations is larger than the average ( $= 24.1 \Omega$ ). In the aqueous LTE,  $R'$  in the top and bottom configurations is larger than the average ( $= 16.1 \Omega$ ). This means that the electrolyte convection has an enhancing effect on  $R_{dif}$ , in addition to the aforementioned suppressing effect.<sup>25</sup> As the

redox reaction progresses, the concentration of reactants/products at the electrode surface changes in a way that prevents further reaction. The resultant concentration gradient drives the diffusion of reactants from (products into) the bulk region, causing  $R_{dif}$ . The electrolyte convection also enhances the mass transfer of the reactants/products, causing the suppressing effect on  $R_{dif}$ . On the other hand, the electrolyte convection tends to make the concentration in the electrolyte uniform and to suppress the concentration gradient in the vicinity of the electrode. This may be the origin of the enhancing effect on  $R_{dif}$ .

## 3 Conclusions

In conclusion, we systematically investigated the resistance components of LTEs composed of aqueous, MeOH and acetone solutions containing  $0.8 \text{ M Fe}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3$ . We found that the  $R_{ct}$  of the MeOH LTE is the smallest among the three LTEs. We demonstrated that the  $W_{max}$  of the MeOH LTE ( $d = 2 \text{ mm}$ ) is slightly larger than or comparable with that of the corresponding aqueous LTE. The MeOH LTE with small  $d$  is a promising LTE candidate with high  $W_{max}$ .

## 4 Experimental section

### 4.1 Coated electrode and electrolyte

Graphite powder (CAS RN: 7782-42-5, Wako Special Grade) was purchased from FUJIFILM Wako Corp. and used as received. The Raman scattering spectrum (Fig. S1†) at room temperature shows two characteristic bands at  $1350 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$ . The former and the latter bands are ascribed to the disorder (D) and graphene (G) bands, respectively. The intensity of the D band is much smaller as compared with that of the G band, indicating a small content of the defects.

The graphite powder and polyvinylidene difluoride (PVDF) were mixed thoroughly in a ratio of 9:1 with  $N,N$ -dimethylformamide (DMF).<sup>28</sup> The mixture was coated onto stainless steel foil (SUS304,  $10 \mu\text{m}$ ) with the use of a coating machine. Then, the electrode was dried in vacuum at  $60 \text{ }^\circ\text{C}$ . The electrode thickness  $t$ , which was evaluated with a micrometer, was controlled by the roll height of the machine. Except for the measurement of the  $t$ -dependence of the resistance components,  $t$  was fixed at  $\approx 100 \mu\text{m}$ . Fig. S2† shows the cross sectional and surface scanning electron microscopy (SEM) images of the electrode ( $t = 131 \mu\text{m}$ ). The electrode consists of graphite particles with uneven surfaces. The size distribution of the particles was determined to be  $19 \pm 12 \mu\text{m}$  from 40 particles.

The electrolytes were aqueous, MeOH, and acetone solutions containing  $0.8 \text{ M Fe}(\text{ClO}_4)_2 \cdot 6.0\text{H}_2\text{O}$  and  $0.8 \text{ M Fe}(\text{ClO}_4)_3 \cdot 7.1\text{H}_2\text{O}$ . The solutes and solvent were purchased from FUJIFILM Wako Corp. and used as received. The solute concentration ( $= 0.8 \text{ M}$ ) was selected because the  $W_{max}$  of the aqueous LTE shows a maximum around  $0.8 \text{ M}$ .<sup>9</sup>



## 4.2 Fabrication of LTE

Resistance and output characteristics of LTE were investigated with a specially-designed two-pole cell (Fig. S3†).<sup>33</sup> The cell consists of a cylindrical electrolyte tank and two electrode plates. The electrolyte tank was a 7.3 mm  $\phi$  polytetrafluoroethylene (PTFE) cylinder. The electrode plate was a 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. The temperatures of the high ( $T_H$ ) and low ( $T_L$ ) electrodes were independently controlled with the Peltier element and cooling fan.  $T_H$  and  $T_L$  were monitored with T-type thermocouples. The electrode area  $s$  was 42 mm<sup>2</sup>. The electrode distance  $d$  was 10 mm or 2 mm.

## 4.3 Device resistance and resistance components

Device resistance, *i.e.*,  $R$  at  $\Delta T = 0$  and  $R'$  at finite  $\Delta T$ , was evaluated from the current  $I$ -voltage  $V$  relation. In the measurement of  $R$ ,  $T_L$  and  $T_H$  were fixed at  $T$ . The slope of the  $I$ - $V$  plot corresponds to  $R$ . The measurement of  $R$  was performed with horizontally oriented LTE (side configuration). In the measurement of  $R'$ ,  $T_L$  was fixed at 298 K. With the open circuit voltage  $V_0$  as the reference,  $V$  changed in proportion to  $I$ . The slope of the  $I$ - $V$  plot corresponds to  $R'$ . We further investigated the orientation and  $\Delta T$  dependence of  $R'$ .

Resistance components, *i.e.*,  $R_s$  and  $R_{ct}$ , were evaluated by electrochemical impedance spectroscopy (EIS) with the use of a potentiostat (Vertex.One.EIS, Ivium Technologies). In the EIS measurement, an alternative electric field is applied, and the induced current component is sensitively detected. The frequency range was from 1 Hz to 20 kHz, and the amplitude was 10 mV. The EIS data were analyzed with a Randles equivalent circuit,<sup>27</sup> which consists of  $R_s$ ,  $R_{ct}$ ,  $C_d$ , and  $Z_W$ .  $Z_W$  is expressed as  $Z_W = A_W(\omega^{-1/2} - i\omega^{-1/2})$ , where  $A_W$  and  $\omega$  are the Warburg coefficient and angular velocity, respectively. Unless otherwise stated, measurement was performed at  $\Delta T = 0$  K and in the side configuration.

## 4.4 Output characteristics of LTE

Output characteristics of LTE were investigated with fixing  $T_L$  at 298 K. The voltage  $V$  was measured against current  $I$  ( $\leq 1.0$  mA).  $W$  is expressed as  $IV$ .  $V_0$  and  $R'$  were evaluated by least-squares fitting of the  $I$ - $V$  plot.  $W_{\max}$  is expressed as  $W_{\max} = \frac{V_0^2}{4R'}$ . To accurately evaluate the convection effect on  $V_0$ ,  $R'$  and  $W_{\max}$ , we carefully investigated their orientation dependence using the same LTE.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

Touya Aiba: data curation; formal analysis; investigation. Haruka Yamada: data curation; formal analysis; investigation (resistance components of MeOH solution against  $t$ ). Yutaka Moritomo: conceptualization; supervision; writing – original draft; writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the Yazaki Memorial Foundation for Science and Technology, the Iwatani Naoji Foundation, and the joint research with Taisei Rotec Corporation.

## References

- 1 T. Ikeshoji, Thermoelectric conversion by thin-layer thermogalvanic cells with soluble redox couples, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1505–1514.
- 2 I. Quickenden and Y. Mua, A review of power generation in aqueous thermogalvanic cells, *J. Electrochem. Soc.*, 1995, **142**, 3985.
- 3 Y. Mua and T. I. Quickenden, Power conversion efficiency, electrode separation, and overpotential in the ferricyanide/ferrocyanide thermogalvanic cell, *J. Electrochem. Soc.*, 1996, **143**, 2558.
- 4 J. Kawamura, M. Shimoji and H. Hoshino, The ionic conductivity and thermoelectric power of the superionic conductor  $Ag_3SBr$ , *J. Phys. Soc. Jpn.*, 1981, **50**, 194–200.
- 5 A. Schiraldi, E. Pezzati and P. Baldini, Thermoelectric power of the high ionic conductivity glasses silver iodide  $AgI: Ag_2O \cdot B_2O_3$ , *J. Phys. Chem.*, 1985, **89**, 1528–1531.
- 6 Y. Liang, J. K.-H. Hui, M. Morikawa, H. Inoue, T. Yamada and N. Kimizuka, High positive seebeck coefficient of aqueous  $\Gamma/I^{3-}$  thermocells based on host-guest interactions and LCST behavior of PEGylated  $\alpha$ -cyclodextrin, *ACS Appl. Energy Mater.*, 2021, **4**, 5326–5331.
- 7 B. Yu, J. Duan, H. Cong, W. Xie, R. Liu, X. Ahuang, H. Wang, B. Qi, M. Xu and L. Wan, Thermosensitive crystallization-boosted liquid thermocells for low-grade heat harvesting, *Science*, 2020, **370**, 342–346.
- 8 Y. Xaing, X. Guo, H. Zhu, Q. Zhang and S. Zhu, Aqueous biphasic-boosted liquid-state thermocell for continuous low-grade heat harvesting, *Chem. Eng. J.*, 2023, **461**, 142013.
- 9 J. H. Kim, J. H. Lee, E. E. Palen, M.-S. Suh, H. H. Lee and R. J. Kang, Iron (II/III) perchlorate electrolytes for electrochemically harvesting low-grade thermal energy, *Sci. Rep.*, 2019, **9**, 8706.
- 10 J. Duan, G. Feng, B. Yu, J. Li, M. Chen, P. Yang, J. Feng, K. Liu and J. Zhou, Aqueous thermogalvanic cells with a high Seebeck coefficient for low-grade heat harvest, *Nat. Commun.*, 2018, **9**, 5146.



- 11 T. Kim, J. S. Lee, G. Lee, H. Yoon, J. Yoon, T. J. Kang and Y. H. Kim, High thermopower of ferri/ferrocyanide redox couple in organic-water solutions, *Nano Energy*, 2017, **31**, 160.
- 12 M. Sindhuja, B. Lohith, V. Sudha, G. R. Manjunath and S. Harinipriya, Low grade thermal energy harvester using graphene-based Thermocells, *Mater. Res. Express*, 2017, **4**, 075513.
- 13 H. Im, T. Kim, H. Song, J. Choi, J. S. Park, R. Ovalle-Robles, H. D. Yang, K. D. Kihm, R. H. Baughman, H. H. Lee, T. J. Kang and Y. H. Kim, High-efficiency electrochemical thermal energy harvester using carbon nanotube aerogel sheet electrodes, *Nat. Commun.*, 2016, **7**, 10600.
- 14 H. Zhou, T. Yamada and N. Kimizuka, Supramolecular thermo-electrochemical cells: Enhanced thermoelectric performance by host-guest complexation and salt-induced crystallization, *J. Am. Chem. Soc.*, 2016, **138**, 10502–10507.
- 15 A. H. Kazim and B. A. Cola, Electrochemical characterization of carbon nanotube and poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) composite aqueous electrolyte for thermo-electrochemical cells, *J. Electrochem. Soc.*, 2016, **163**, F867.
- 16 S. W. Lee, Y. Yang, H.-W. Lee, H. Ghasemi, D. Kraemer, G. Chen and Y. Cui, An electrochemical system for efficiently harvesting low-grade heat energy, *Nat. Commun.*, 2014, **5**, 3942.
- 17 Y. Tanaka, A. Wake, D. Inoue and Y. Moritomo, Concentration gradient effect in liquid thermoelectric device composed of organic-solvent-added aqueous solution containing  $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ , *Jpn. J. Appl. Phys.*, 2024, **63**, 014002.
- 18 A. Wake, D. Inoue and Y. Moritomo, A liquid thermoelectric device composed of organic solution, *Appl. Phys. Express*, 2022, **15**, 054002.
- 19 A. Wake, D. Inoue and Y. Moritomo, Liquid thermoelectric conversion devices composed of several organic solvents, *Jpn. J. Appl. Phys.*, 2023, **62**, 014002.
- 20 K. Kim, S. Hwang and H. Lee, Unravelling ionic speciation and hydration structure of Fe(III/II) redox couples for thermoelectrochemical cells, *Electrochim. Acta*, 2020, **335**, 135651.
- 21 M. A. Buckingham, F. Marken and L. Aldous, The thermoelectrochemistry of the aqueous iron(II)/iron(III) redox couple: significance of the anion and pH in thermogalvanic thermal-to-electrical energy conversion, *Sustainable Energy Fuels*, 2018, **2**, 2717–2726.
- 22 S.-M. Jung, S.-Y. Kang, B.-J. Lee, J. Kwon, D. Lee and Y.-T. Kim, Fe-N-C electrocatalyst for enhancing Fe(II)/Fe(III) redox kinetics in thermo-electrochemical cells, *Adv. Funct. Mater.*, 2023, **33**, 2304067.
- 23 B. Yu, H. Xiao, Y. Zeng, S. Liu, D. Wu, P. Liu, J. Guo, W. Xie, J. Duan and J. Zhou, Cost-effective n-type thermocells enabled by thermosensitive crystallizations and 3D multi-structured electrodes, *Nano Energy*, 2022, **93**, 106795.
- 24 J. Duan, B. Yu, L. Huang, B. Hu, M. Xu, G. Feng and J. Zhou, Liquid-state thermocells: Opportunities and challenges for low-grade heat harvesting, *Joule*, 2021, **5**, 768–779.
- 25 W. Yang, L. Sun, J. Bao, Z. Mo, M. Du, Y. Xu and J. Zhang, Multiphysics modeling of mass and heat transfer in a thermo-electrochemical cell, *Ind. Eng. Chem. Res.*, 2023, **62**, 12345.
- 26 P. F. Sadazar, S. Kumar and B. A. Cola, Design and optimization of thermo-electrochemical cells, *J. Appl. Electrochem.*, 2014, **44**, 325–336.
- 27 A. J. Bard, L. R. Faulkner and H. S. White, *Electrochemical Methods*, Wiley, West Sussex, 2022.
- 28 T. Aiba, D. Inoue and Y. Moritomo, Coated electrodes for liquid thermoelectric conversion devices to enhance  $Fe^{2+}/Fe^{3+}$  redox kinetics, *Sustainable Energy Fuels*, 2024, **8**, 2138–2143.
- 29 P. Connor, J. Schuch, B. Kaiser and W. Jaegermann, The determination of electrochemical active surface area and specific capacity revisited for the system  $MnO_x$  as an oxygen evolution catalyst, *Z. Phys. Chem.*, 2020, **234**, 979–994.
- 30 R. Martínez-Hincapié, J. Wegner, M. U. Anwar, A. Raza-Khan, S. Franzka, S. Kleszczynski and V. Čolič, The determination of the electrochemically active surface area and its effects on the electrocatalytic properties of structured nickel electrodes produced by additive manufacturing, *Electrochim. Acta*, 2024, **476**, 143663.
- 31 H. Tian, C. Chen, Z. Yu, W. Luo, X. Yu, Z. Chang, S. Li, X. Cui and J. Shi, Controlled construction of core-shell structured prussian blue analogues towards enhanced oxygen reduction, *ChemSusChem*, 2024, **17**, e202301265.
- 32 K. Nishitani and Y. Moritomo, Thermal conductivity of organic solutions against solute concentration, *J. Phys. Soc. Jpn.*, 2024, **93**, 045002.
- 33 Y. Fukuzumi, Y. Hinuma and Y. Moritomo, Configuration entropy effect on temperature coefficient of redox potential of  $P2-Na_xCoO_2$ , *Jpn. J. Appl. Phys.*, 2019, **58**, 065501.

