

Master's Thesis  
석사 학위논문

Highly efficient thermogalvanic cells based on  
iodide/triiodide redox couple in carbonate solutions

Kyunggu Kim(김 경 구 金 慶 求)

Department of Energy Systems Engineering  
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A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Master of Science. The study was conducted in accordance with Code of Research Ethics<sup>1</sup>

11. 15. 2013

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<sup>1</sup> Declaration of Ethical Conduct in Research: I, as a graduate student of DGIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, and distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.

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김 경 구

Accepted in partial fulfillment of the requirements for the de-  
gree of Master of Science

11. 15. 2013

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### ABSTRACT

Around the globe, a demand of the gasoline and electricity is elevated and also prices of them are increasing. A lot of wasted thermal energies (below 100°C) all over the world have been recycled such as geothermal, sun light, power plants, and engines. To decrease the carbon emissions from utilizing fossil fuels, wasted low grade heat energies can be alternative on underground resources; coal, petroleum, natural gas.

Thermo-galvanic (TG) cell is electrochemical cell in which the identical electrodes are held in electrolyte at different temperature. It converts thermal energy to electric energy directly without carbon emission, utilizes the ambient low grade heat under 100°C, and has very simple design. Liquid-based thermo-electro-chemical technologies offer an alternative, potentially cheaper and more scalable route for direct thermal-to-electric energy conversion with no carbon emissions. In this study, to find out the maximum values of power conversion efficiency(PCE), Seebeck coefficient (SC) and Output power, we utilize numerous concentrations of  $I_3^-/I^-$  redox couple by mixing various volume ratios of solvents such as EC (ethylene carbonate), DEC (diethyl carbonate), EMC (ethyl methyl carbonate), and DMC (dimethyl carbonate). We also experiment the existing aqueous system of TG cell with some changes such as electrode area and temperature difference to make same conditions with our organic TG cell, and display the aqueous TG cell to compare with our organic TG cell after optimizing the PCE, SC, and output power. The PCE with MWNT electrodes / Carnot efficiency is shown to be 1.4 % in the literature, which is the highest one in the current field of TG cell. In our study, we found 4.83 % of PCE/ Carnot efficiency at 1.2 M  $I_3^-/I^-$  redox couple in EC/DMC (0.25/9.75, v/v %).

Keywords: thermo-galvanic cell, iodide based redox couple, carbonate system solvents, Seebeck coefficient, Power conversion efficiency.

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# I . INTRODUCTION

Around the globe, a demand of the gasoline and electricity is elevated and also prices of them are increasing [1]. Thus, alternative energy sources have to be found to solve those problems.

A lot of thermal energies (below 100 °C) all over the world have been wasted such as geothermal, sun light, power plants, and engines[2]. Wasted low grade heat energies can be alternative on underground resources such as coal, petroleum, natural gas which make the carbon emission problems.

Research on energy converting from thermal energy to electrical energy have been conducted for the last thirty years, and thereby there are many generators to make electricity by utilizing heat such as thermoelectric, thermogalvanic, and thermalionic, solar thermal generator.

Until now, to change heats to electricity, thermo-electric devices have been widely researched with regard to semiconductors having low band gap like bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ), antimony telluride ( $\text{Sb}_2\text{Te}_3$ ) [3], and thermo-electrics (TE) have been extensively studied with big interests for applications such as power generators, sensors, coolers because of the extraordinary advantages for instant and simple process, small size, long lifetime and simple operation.

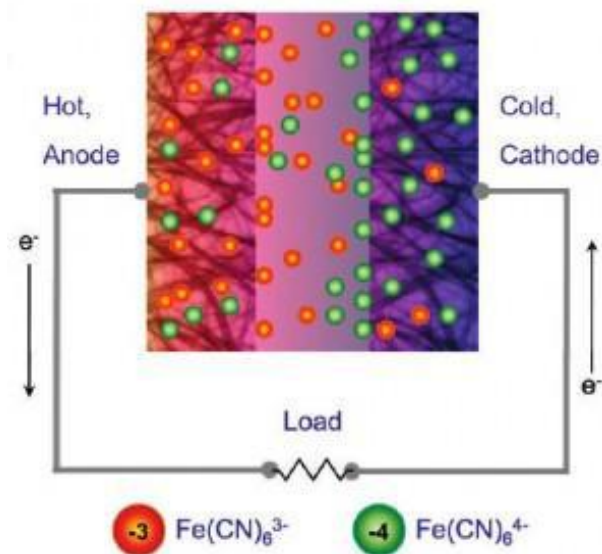
However, TE has a little of disadvantages such as the large thermal conductivity and low Seebeck coeffi-

cient (SC) because of high electric conductivity, and materials of TE have expensive production cost [4].

Thermo-galvanic (TG) cell is electrochemical cell in which the identical electrodes are held in electrolyte at different temperature [5]. It converts thermal energy to electric energy directly without carbon emission, utilizes the ambient low grade heat under 100°C, and has very simple design. Liquid-based thermo-electrochemical technologies offer an alternative, potentially cheaper and more scalable route for direct thermal-to-electric energy conversion with no carbon emissions.

The TG cell is currently promising, suitable, and sustainable for making electricity by utilizing the wasted heats because of some advantages; simplicity of device fabrication, long lifespan, noiseless and non-dynamic operation process.

The TG cell which utilized  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox couple in aqueous solutions has been widely researched due to the large reaction entropy and fastest charge transfer reaction; low charge transfer resistance, high reversibility[1,5-9]. However, this system has a problem such as limitation of operating temperature ranged from 0 to 100 °C because of a solidification and evaporation of aqueous solutions.



**Fig. 1.  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox TG cell**

The principle of TG cell can be explained by the dependence of oxidation and reduction potential which results from temperature gradient between cold electrode and hot electrode. In case of a  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox couple in aqueous solution, oxidation reaction (anode) occurs at the hot side and then the electrons move into cold side (cathode) throughout out circuit. At the same time, ions at cold side go to hot side throughout electrolyte shown in Figure 1. Meanwhile, electrons move into hot side from cold side in case of iodide based  $\text{I}_3^-/\text{I}^-$  redox couples in carbonate solvent systems as shown in figure 2.

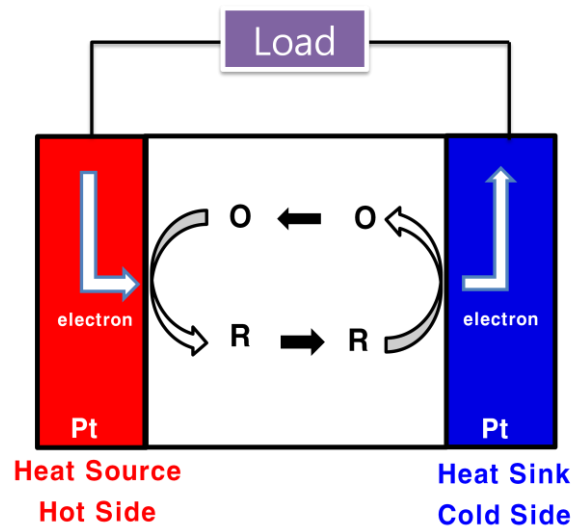


Fig 2.  $I_3/T$  redox TG cell

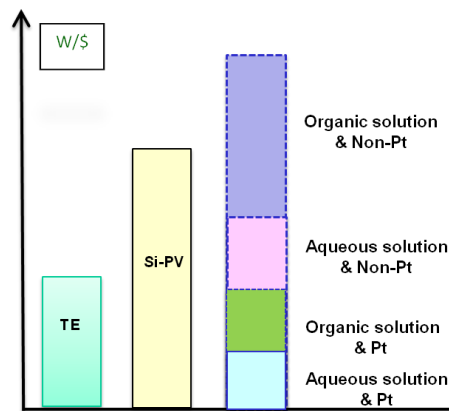


Fig 3. Cost-effect on TE, PV, and TG.

Type	Materials	Temperature	Seebeck coefficient	Electric conductivity	Thermal conductivity	ZT	Carnot Efficiency	\$/W
		K	mV/K	S/cm	W/m/K			
TE	$Bi_2Te_3$	300	0.25	1000	2	0.94	15.3	0.4-59
TG	Aqueous / Pt	300	1.4	0.6	0.6	0.06	0.6	50
	Aqueous / CNT					-	1.4	3-5
	Organic / Pt	300	7	0.012	0.17	0.10	1.6	20

Table 1. Comparison of properties on thermal energy harvesting devices

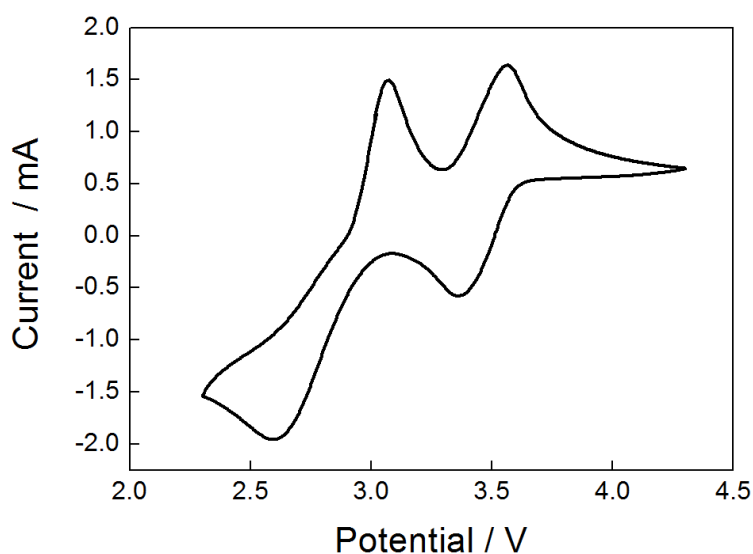
TG cells, once actively researched in 1980s, were stagnated since the cost for TG cell is higher than that of Silicon Photovoltaic (Si-PV) cells. However, recent progress in material science and electrochemistry has en-

abled TG cells to be competitive compared with Si-PV cells, which is reviving the world-wide R&D activities on TG cells.

$I_3^-/I^-$  redox couple as shown in figure 4 which is well-known redox couple in the DSC research fields is utilized as roles of bulk charge transport, and interfacial charge transfer at surfaces of photo-anode and cathode.

The properties of them are extensively researched and reported from DSC researcher.

EC, DMC, EMC and DEC which is well-known organic solvents were investigated in secondary battery fields as the ion pathway of electrolyte. Also, the properties were reported at various conditions.



**Fig. 4. Cyclic Voltammetry of  $I_3^-/I^-$  redox couple**

This study aims are to check the tendency of data on results by changing concentration and temperature gradient on  $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$  redox couple in aqueous solution, and to increase the power conversion efficiency (PCE), Seebeck coefficient (SC), and Output power, we utilize numerous concentrations of  $I_3^-/I^-$  redox couple by mixing various volume ratios of solvents such as EC, DEC, EMC and DMC. After we attempt to

optimize the PCE, SC, and power, those results are compared with aqueous system TG cell, and then the reasons for the results were analyzed. We made an effort to find out clarification by measuring ionic conductivity and viscosity for various temperature conditions. We also tried to find structure formation between the  $I_3^-$ ,  $I^-$  and solvents at high temperatures (hot side Temp. = 60 °C). Additionally, the properties according to cell shape are studied such as U and I-shaped cells. Thermal conductivity was investigated on 0.5 and 1 M concentration of  $I_3^-/I^-$  redox couple in EC/DEC and EC/DMC by changing temperature gradient.

## II . THEORITICAL BACKGROUND

### 2.1. Seebeck coefficient

The electrochemical Seebeck effect was first demonstrated over 100 years ago [10]. The Seebeck effect which is named by the Baltic German physicist, Thomas Johann Seebeck in 1821 means the conversion of temperature differences directly into electricity and [2,11]. When two metals are contacted at different temperature, potential is generated because the metals responded differently to the temperature difference, creating a current loop and a magnetic field. This can be expressed as the ways of thermo-galvanic cell performance, and in general , in case of the redox reaction in thermo-galvanic, on  $a+ne \leftrightarrow b$

$$S = \frac{\partial V}{\partial T} = \frac{\Delta S_{a,b}}{nF} \quad 1)$$

Where  $\Delta S_{a,b}$  is the reaction entropy difference of species a and b from hypothetical redox reaction, F is Faraday constant, V is Potentials, T is temperature, and n is a number of electron.

Aqueous  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  system which is higher reversible system has Seebeck coefficient values of  $>1\text{mV/k}$ . when cobalt (II/III) in ionic liquid system is used, Seebeck coefficient value was reported up to  $2.2\text{mV/k}$ .



## 2.2 Figure of Merit and Power conversion efficiency

The efficiency of thermo-electric device and thermo galvanic cell are conventionally judged by dimensionless figure of merit [2]. That is expressed by

$$Z=(\partial V/\partial T)^2\alpha/k \quad 2)$$

Where  $\partial V/\partial T$  is Seebeck coefficient,  $\alpha$  is electric conductivity,  $k$  is thermal conductivity.  $\alpha/k$  is the relation on electric and thermal conductivity during thermo-galvanic cell operation. In case of thermo-galvanic cell, the charge carriers are ions, and the behavior of these ions between hot electrode and cold electrode contributes to the ionic conductivity. The thermal conductivity value is affected by the behaviors of charge carriers (ions) in redox couple and solution. At the electrolyte media, thermal conductivity is less than that of metal and semi-conductor.

Power conversion efficiency (PCE) can be expressed as

$$\phi = \frac{\frac{1}{4} V_{oc} I_{sc}}{Ak(\frac{\Delta T}{d})} \quad 3)$$

where  $V_{oc}$  is open circuit voltage,  $I_{sc}$  is short circuit current,  $A$  is the area of electrode,  $k$  is thermal conductivity,  $\Delta T$  is temperature difference between hot and cold electrode,  $d$  is the distance of electrode from hot to cold side. The numerator of above equation can be considered as the maximum output power from system which is the highest point of power-current curves[12]. The nominator indicates the input thermal energy for maintain-

ing constant temperature difference of hot electrode and cold electrode. Hence, PCE means how much amount of electric power can be obtained from the input thermal energy.

### 2.3 Soret effect

The Soret effect which was discovered by the Swiss scientist Charles in 1879 is utilized to verify the existence of a concentration gradient due to the diffusion flux of ions in the electrolyte caused by the temperature gradient at each side[14]. When the temperature gradient exists from cold side and hot side in U-shaped cell, the heat flux occurs from hot to cold side because the velocity of ions depends on the temperature (ions at the hot side move much faster than ions at the cold side).

### 2.4 Cyclic voltammetry

Cyclic voltammetry (CV) is the most popular electrochemical analysis technique. By using this technique, oxidation - reduction potential and reversibility of redox couple can be found out. Three electrode systems (working, counter and reference electrode) were introduced to conduct this technique.

### 2.5 Operation mechanism

TG cell is electrochemical cell in which the identical electrodes are held in electrolyte at different temperature [5]. It converts thermal energy to electric energy directly without carbon emission, utilizes the ambient low grade heat under 100 °C. When the temperature gradient was made between the hot and cold electrode, a

redox potential difference was generated. If the hot and cold side is connected to an external electrical load, electrons are moved throughout the external circuit from high to low Fermi level. At the same time, ions are also migrated from one to another side, and therefore the electric powers can be generated.

At an interface between an electrode and electrolyte, Fermi energy can be thermodynamically determined by the interaction of electron of electrode material with electron of electrolyte molecular orbital at a particular temperature to make a stable state.

### III. Experimental

#### 3.1. Electrode

Platinum electrodes were prepared from 99.99% pure Pt sheet of 0.1mm thick. Pt wire was made from 99.95% pure Pt wire of diameter of 0.5mm. Those materials were purchased from Sigma-Aldrich Company. Spot welding was conducted on this platinum sheet whose area was 1.54cm<sup>2</sup> with platinum wire of 7 cm to make external circuit.

#### 3.2 Electrolyte

The redox couple of Fe(CN)<sub>6</sub><sup>4-</sup>/Fe(CN)<sub>6</sub><sup>3-</sup> was prepared from Potassium hexacyanoferrate(II) trihydrate and Potassium ferricyanide(III) from Sigma-Aldrich Company. The concentrations of this system were 0.06, 0.16, 0.26, 0.36, 0.46 M (mol/L). Those salts were easily dissolved in an aqueous ambient due to high dielectric constant of H<sub>2</sub>O.

In the case of organic systems, The lithium iodide and iodine were purchased from Sigma-Aldrich Company. As organic solution, the EC, DEC, EMC and DMC which were well-known solvents in Li-ion secondary batteries were utilized as mixture of EC/LC (v/v %) system. To make I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple, lithium iodide concentration has to be two times higher than Iodine (2/1).

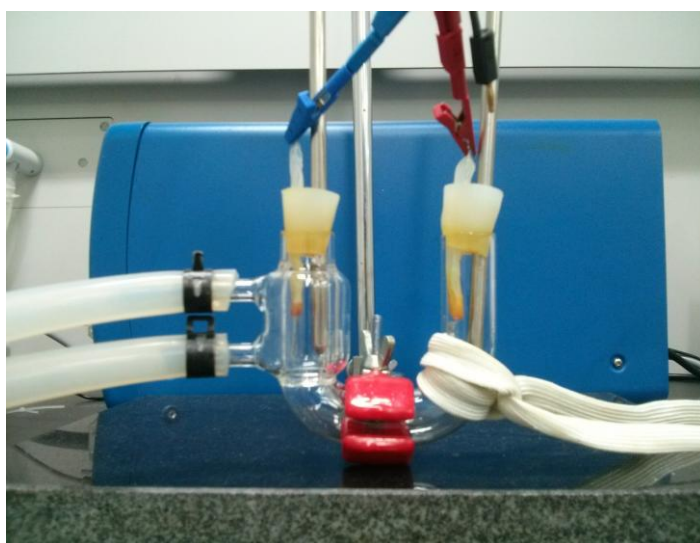


In case of 1 M  $I_3^-/I^-$  redox couple, lithium iodide of 2 M and iodine of 1 M were put into organic solution. Iodide in 1 M of lithium iodide is reacted with iodine, and changed to triiodide because of big equilibrium constant as shown in equation 4. The various concentrations from 0.5M to 1.5M were made by changing volume fraction of linear carbonate and cyclic carbonate (EC/DMC, v/v %). Mixed solutions with iodide based redox couple are stirred with magnetic bar on magnetic stirring palettes for three hours.

### 3.3 preconditioning process

All platinum electrode sheets are polished by alpha alumina whose particle size is  $0.3\mu\text{m}$  on polishing pad for 15 minutes, Those electrodes are then washed in ultrasonic cleaner during five minutes. To eliminate water on electrodes, platinum sheets are dried in oven of  $60^\circ\text{C}$ .

### 3.4 Power properties and open circuit voltage measurements



**Fig. 5. Image of U-shape experimental set up on TG cell**



**Fig. 6. Image of I-shape experimental set up on TG cell**

To make the temperature difference between hot and cold electrode, the hot side temperature is controlled using electric heating tape connected to a temperature controller and the temperature of cold side is changed by circulating water bath. Temperature of hot and cold side is monitored by digital multi-meter linked to K-type thermo-couple.

The identical platinum electrodes are held in prepared electrolyte, and the temperature difference is 35 °C.

Open circuit voltage and power properties are measured by Potentiostat (model: SP-200) from Bio-Logic SAA. To measure power properties, the chronopotentiometry method is applied.

## IV. RESULT AND DISCUSSION

### 4.1 $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ redox couple in aqueous solution

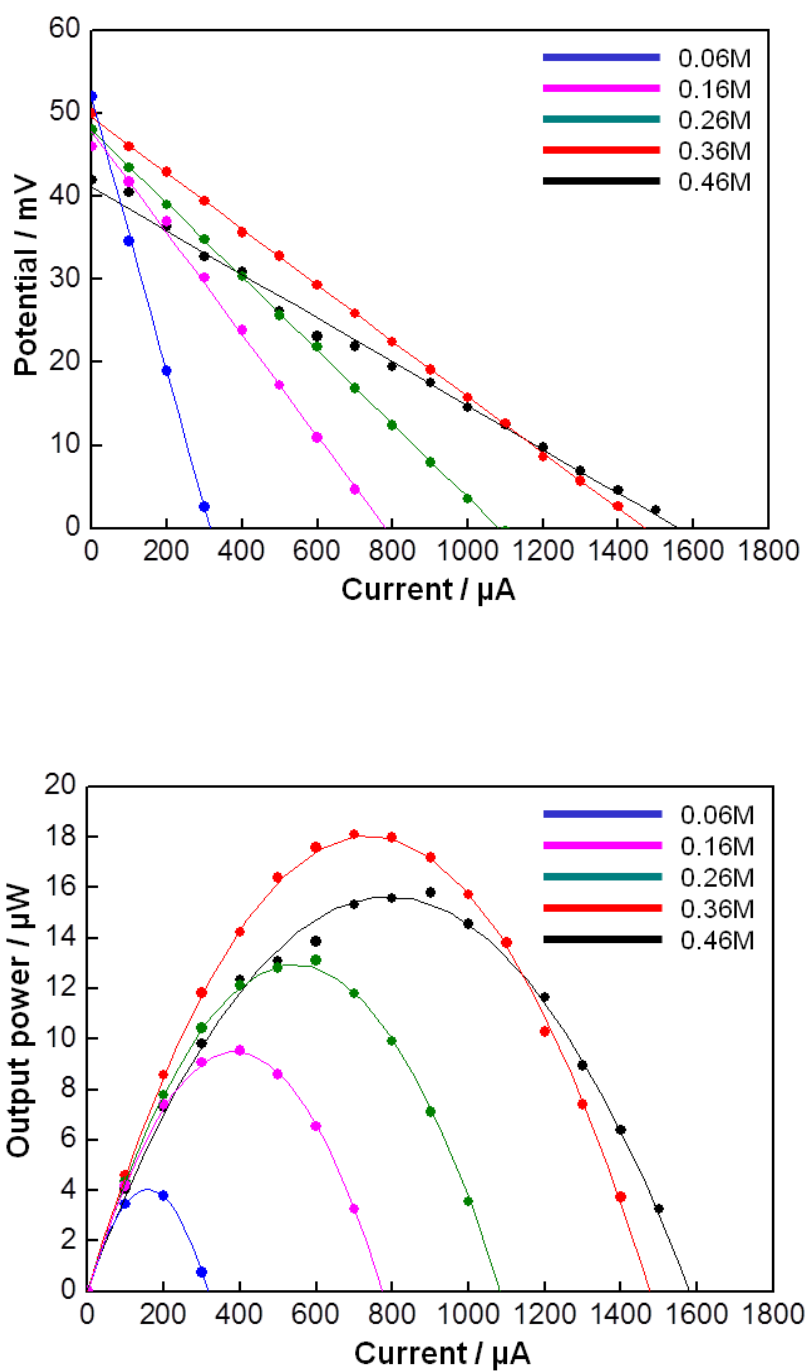
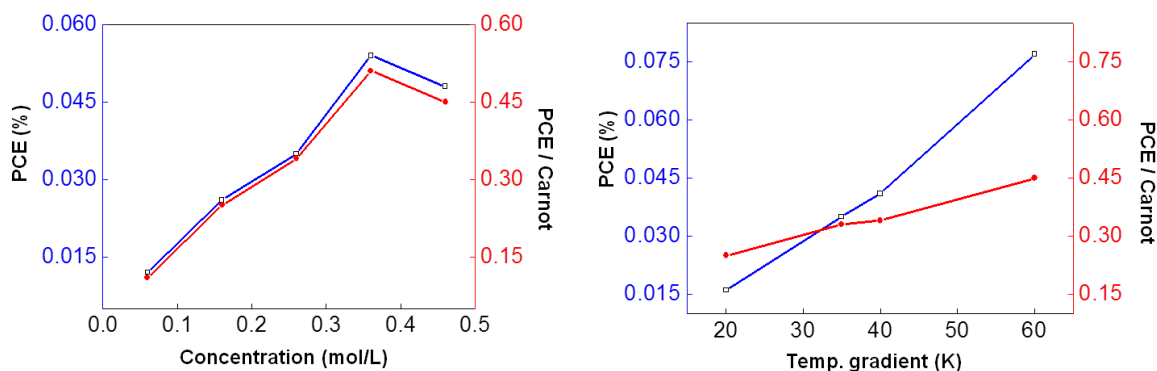


Fig. 7. The effects of concentrations on cell potentials (above) and power output (below)



**Fig. 8. PCE and PCE/Carnot at increasing concentrations (left) and temperature gradients (right)**

There are three types of resistances in electrolyte media such as charge transport resistance, ohmic loss, and mass transport resistance. The charge transport resistance is related to redox reaction which is electron transference at electrode surface. The ohmic loss is concerned with electric resistance. The mass transport resistance is due to absence of reactant at vicinity of electrode, which decreases as the concentration increases.

Those three kinds of resistances contribute to the ionic conductivity value.

The electrochemical characteristics of aqueous TG cell by changing concentration from 0.06 to 0.46 M were investigated. Figure 7 indicates the cell potentials and power outputs by increasing concentration. As the concentration increases, the short circuit current also increases from 300 to 1600  $\mu\text{A}$ . Since the electrolyte resistance decreases as the concentration increases to a certain point, the ionic conductivity can increase in electrolyte, and ions for redox reaction at the electrode surface can be abundant. Thus, the short circuit current can be maximized at that certain point.



The open circuit voltages increases slightly by changing the concentration from 0.06 to 0.46 M. The Seebeck coefficient is inversely proportional to the electrical conductivity. At the 0.06 M concentration of  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  in aqueous solutions, the open circuit voltage is 34 mV. In case of 0.46 M, open circuit voltage was equal to 45 mV.

Figure 7 shows the relation between the output power and current density. The output power, which is calculated by multiplying potential and current, increases as the concentration increases. Maximum output power is 18  $\mu\text{W}$  for 0.46 M of  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox couple in aqueous solutions.

Figure 8 (left) indicates the power conversion efficiency and power conversion efficiency against Carnot efficiency according to concentration of  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  in aqueous solutions. Up to 0.36 M of this system, PCE increases since the current density becomes larger from variation of charge carrier concentrations. However, it decreases from the certain point because of larger viscosity.

Figure 8 (right) shows a diagram of PCE and PCE/Carnot by changing temperature gradient  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  systems in aqueous solutions. PCE increases as the gradient of temperature gets higher. The open circuit potential is clearly proportional to the temperature gradient, and the trends of output power is also similar with them. It means higher temperature gradient causes the decrement of internal resistance due to higher activity of charge carriers. As a result, PCE becomes larger. The movements of charge carriers in TG cell are

classified into migration, diffusion and convection. Most decisive movement of major charge carriers is convection rather than any others. The convection effect becomes much bigger as the temperature gradient gets larger.

#### 4.2 $I_3^-/I^-$ redox couple in organic solution

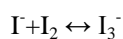
Figure 9 explains the effect of the cell shapes. (a) and (b) are I-V and output power curves of U shaped TG cell. The distance between two electrodes is 9.5 cm for the U-shaped cell. (c) and (d) indicate I-shaped cell with 3 cm distance between hot and cold side. In case of U-shaped cell, OCV is 246 mV. It is higher than 208 mV of I-shaped cell. In iodide based TG system with 1.2 M of  $I_3^-/I^-$  redox couple, OCV value is ranged from 205 to 260 mV.

One of affecting factors for SCC value is the electrolyte resistance in the cell. SCC value is dependent on the distance of two electrodes from each side. I-shaped cell has smaller distance than U-shaped cell. It means that the resistance of I-shaped cell is lower than that of U-shaped cell. Additionally, in case of I-shaped cell, the displacement of hot side is under than that of cold side. Thus, the convection of electrolyte can easily occur rather than the cell whose displacement of each side is reversed.

To overcome the limitations of  $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$  aqueous systems, the TG cell experiments based on  $I_3^-/I^-$  redox couples in carbonate systems are underway in this study. The present statuses of the iodide-based TG

cell were then assessed by changing temperature gradients between the cold and hot sides, electrolyte concentrations, and linear carbonate volume ratios against cyclic carbonates.

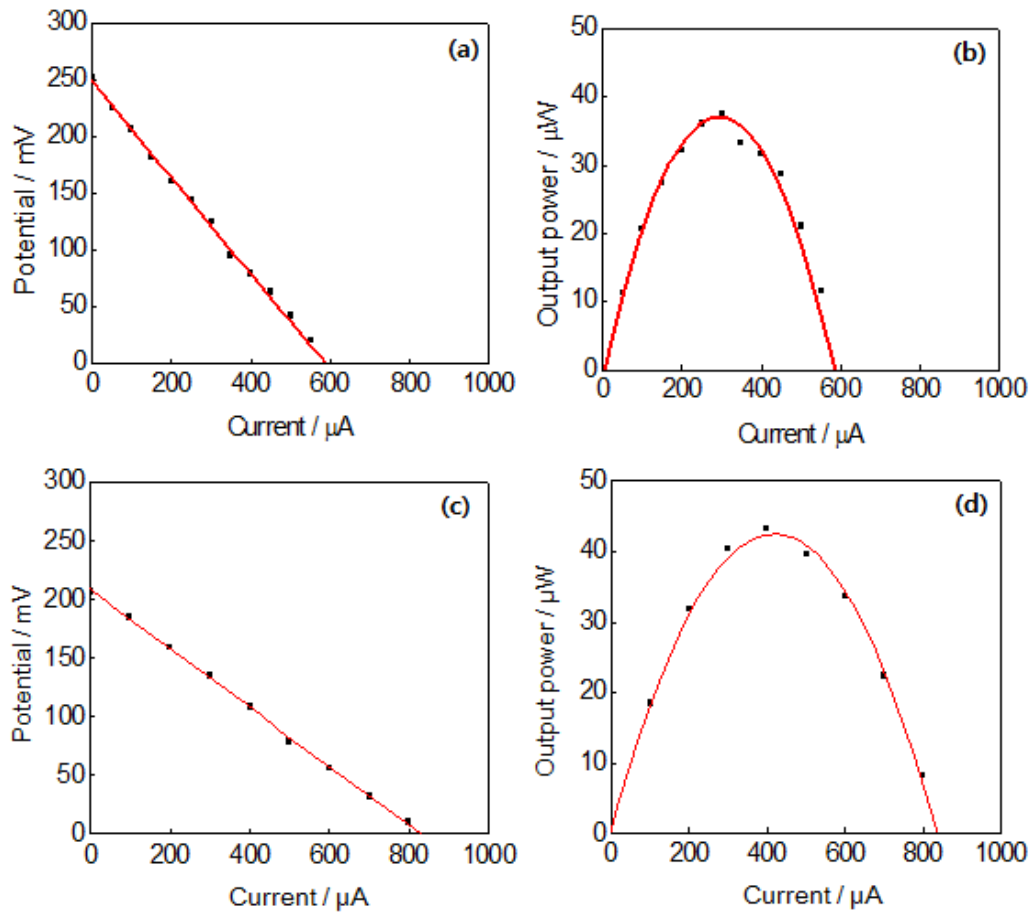
To make  $I_3^-/I^-$  redox couple, 2/1 ratio of  $LiI/I_2$  was employed from the below reactions.



There are two kinds of solutions for TG cell: aqueous and organic solutions. Regardless of the types of solutions, the electrolyte should have lower thermal conductivity to maintain the temperature gradient between hot and cold electrodes. Furthermore, the ionic conductivity of electrolyte also has to be maximized to increase current density.

Since the reagents are well dissolved in solvents such as EC and DMC which are commonly used in the Li-ion secondary batteries, those solvents have suitable dielectric constants.

Finally, the solutions must have high boiling point to work well in the operation temperature of TG cell.



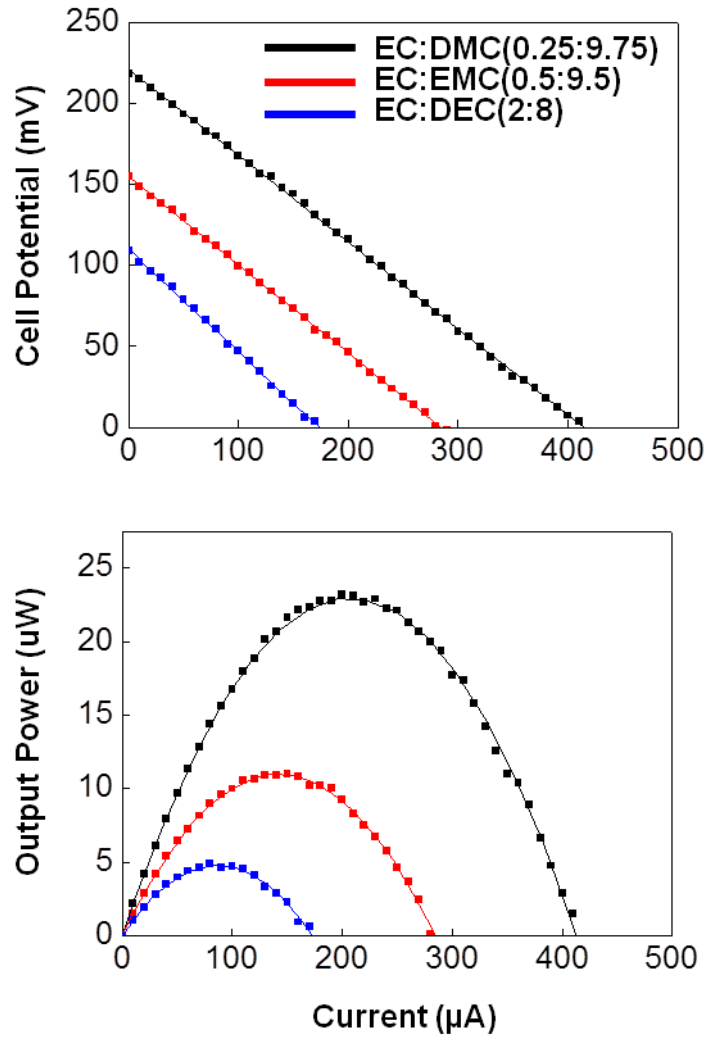
**Fig. 9. Comparisons of I/V and Power on U(a, b) and I (c, d) shape cell**

The electrolyte resistance is the most important property on TG cell. As mentioned above, the charge carriers can be migrated by the diffusion, convection, migration from one electrode to another electrode. In general electrochemical cell, the diffusion (mass transference from bulk of electrolyte to electrode surface) dominates a current performance in solutions. On the other hand, the ions' movements of redox couple are minor affected by the migration and convection.

In contrast, For TG cell systems, the thermal diffusion can be made by a concentration distinction at a hot and cold position to maintain thermodynamically homogenous electrolyte. The convectonal mass transport can be generated by density and temperature differences. Convection is especially useful among those three movements of ions in TG cell. It is affected by geometrical cell shape. Hence, the cell shape is particular pa-

rameter on TG cell. Current performance was studied by virtue of cell shape; U-shaped and I-shaped cell.

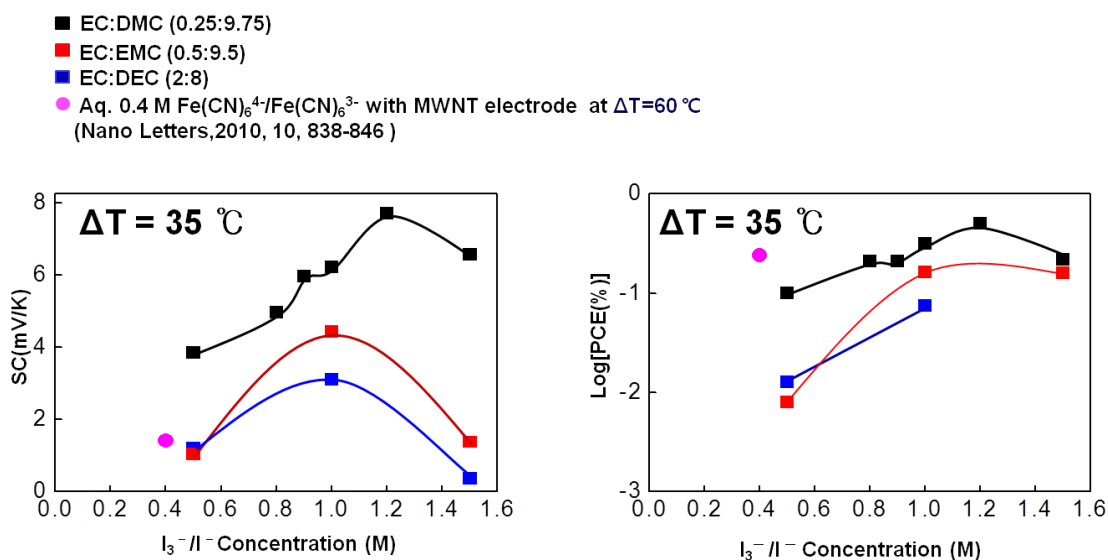
The cell potentials of U-shaped cell were higher than those of I-shaped cell, and the currents of I-shaped cell were higher than those of U-shaped cell.



**Fig. 10. Cell potentials (above) and power output (below) on DMC, EMC, DEC at  $\Delta T=35$ , 1M**

TG experiments were conducted at  $\Delta T$  35 between the cold and hot sides in 1 M  $I_3^-/I^-$  in EC/DMC (0.25/9.75, v/v), EC/EMC (0.5/9.5, v/v), and EC/DEC (2/8, v/v) solutions to examine the cell potentials and power outputs, and the results are shown in figure 10. EC/DMC (0.25/9.75, v/v) electrolyte system is the best optimized

one as compared with EC/DEC (2/8, v/v) and EC/EMC (0.5/9.75, v/v). At this system, OCV increases up to 218 mV, SCC is 413  $\mu$ A, and Output power is 23  $\mu$ W.



**Fig. 11. SC (left) and log [PCE (%)] (right) of  $\text{I}_3^-/\text{I}^-$  redox couple at changing concentration**

The experiments shown in figure 11 were conducted to evaluate a cell performance with various concentrations. In case of SC values, they were elevated by increasing concentration up to 1 M (EMC, DEC) and 1.2 M (DMC), and then decrease. They are two times to four times higher than those in aqueous systems.

As shown in Figure 11, PCE values also increase by elevating electrolyte concentrations up to particular points (EMC, DEC) - 1 M, (DMC) - 1.2 M. At  $\text{I}_3^-/\text{I}^-$  1.2M in EC/DMC (0.25/9.75, v/v). We analogize that this phenomenon is mainly due to interactions between linear carbonate and iodide.

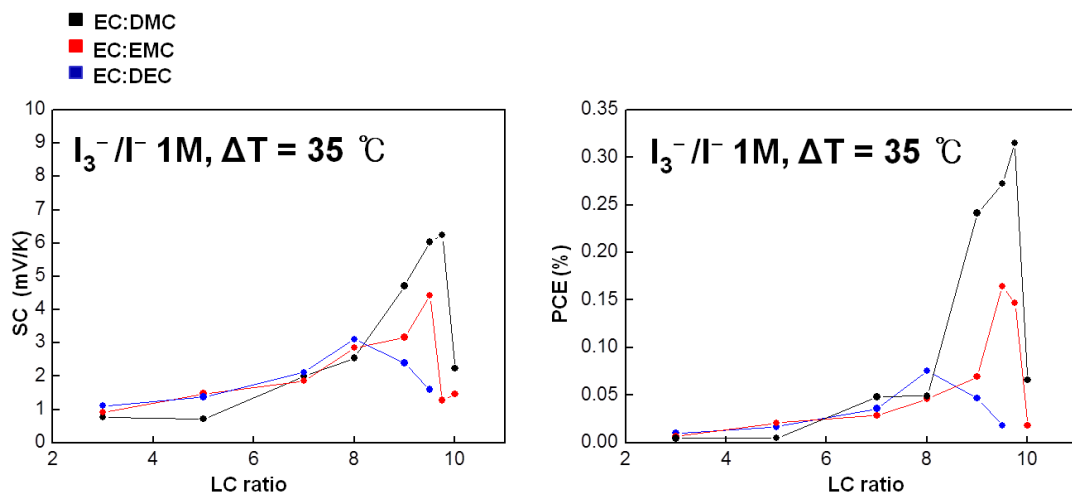


Fig. 12. SC (left) and PCE (right) at changing LC volume ratio (EC/LC)

- 1.2 M EC:DMC (0.25:9.75)
- 1.0 M EC:EMC (0.5:9.5)
- 1.0 M EC:DEC (2:8)
- Aq. 0.4 M  $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$  with MWNT electrodes at  $\Delta T=60^\circ C$  (Nano Letters, 2010, 10, 838-846)

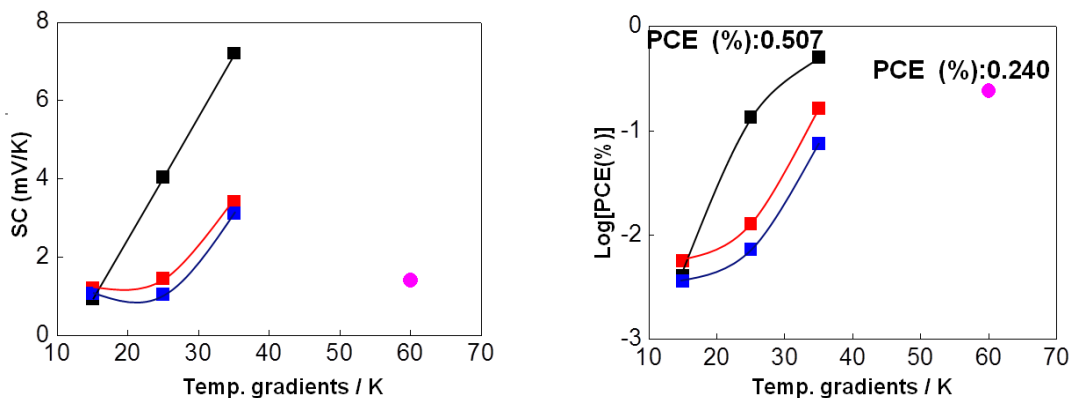


Fig. 13. SC (left) and  $\log [PCE (\%)]$  (right) of  $I_3^-/I^-$  redox couple at changing Temp. gradients

TG experiments in figure 12 were conducted to check the LC effect in the electrolyte. The relationship of cell performances and  $\Delta T$  were investigated by elevating the temperature gradient between the hot and cold side. SC and PCE were studied by increasing temperature gradients from  $15^\circ C$  to  $35^\circ C$  with iodide based 1.2

M salts in EC/DMC, 1 M EC/EMC, and 1 M EC/DEC. The temperature gradient can be made up to 35°C because evaporation problem can occur at hot side temperature.

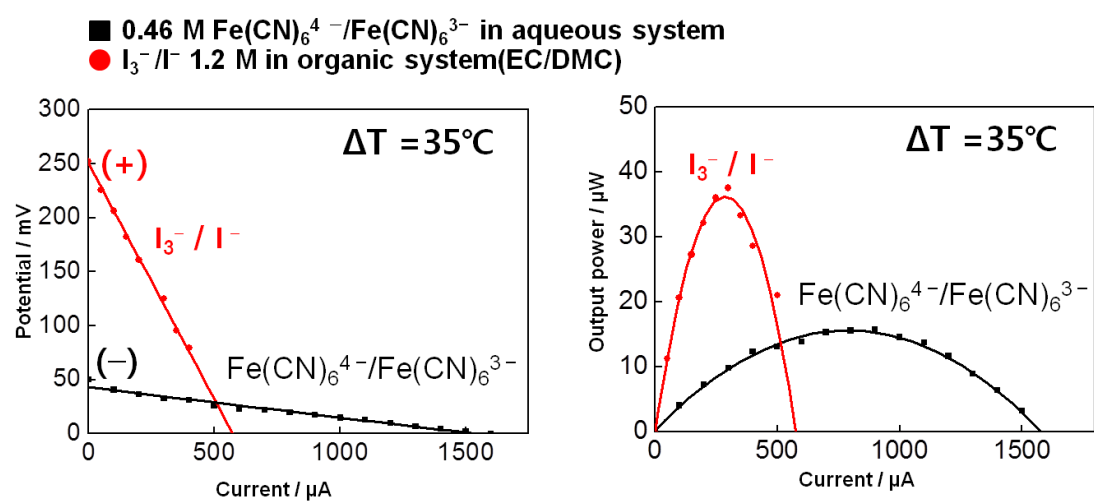
When temperature difference increases, SC and PCE values were also elevated because of an enhanced interaction of linear carbonate and iodide at a hot side. The maximum SC and PCE value were obtained at 1.2 M EC/DMC (0.25/9.75, v/v) solutions as shown in figure 13.

#### 4.3 Comparison of aqueous and organic solution systems

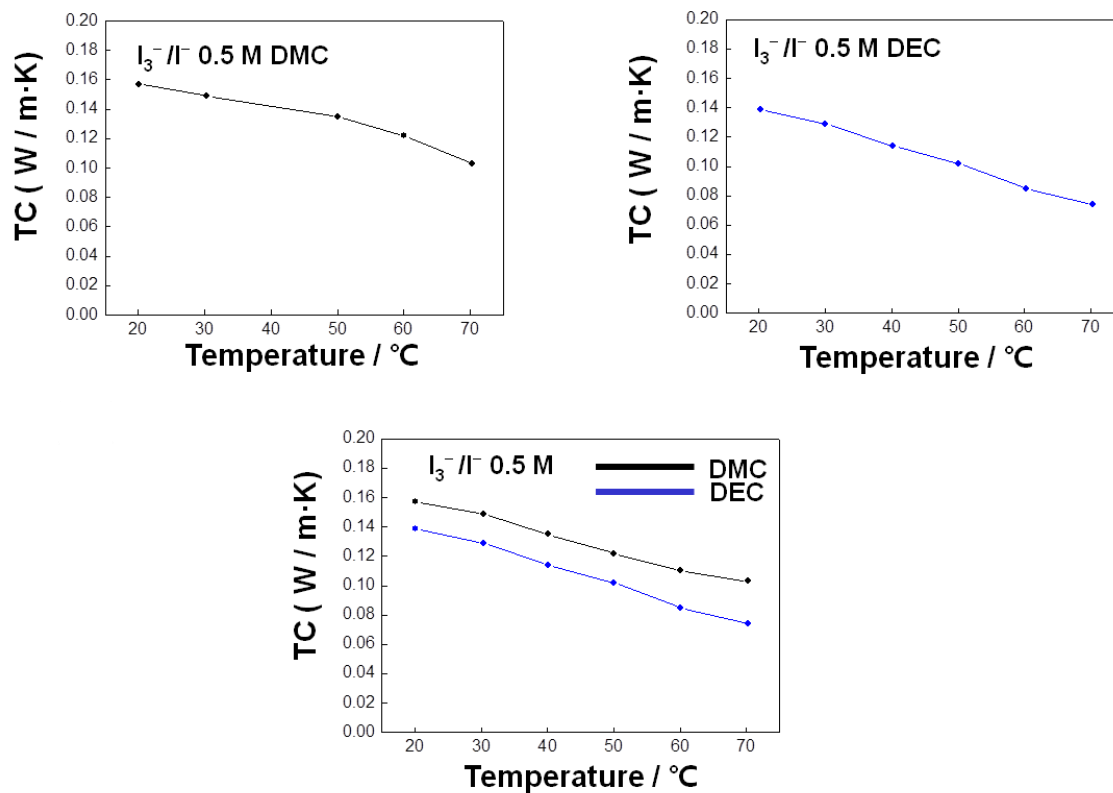
The comparison of power properties on organic and aqueous systems was conducted as shown in figure 14. OCV of 1.2 M  $I_3^-/I^-$  in organic systems (EC/DMC) is higher than aqueous systems. That is, SC value of organic system is higher as compared with aqueous one.

Electrolyte resistance can be explained by the current property. SCC of aqueous systems is lower than organic one. It means that aqueous system has lower electrolyte resistance. Output power can be calculated by multiplying potential and current. Maximum power of organic system is 38  $\mu$ W. This value is two times higher than that of aqueous system.





**Fig. 14. Comparisons of cell potentials and power outputs on aqueous and organic TG**



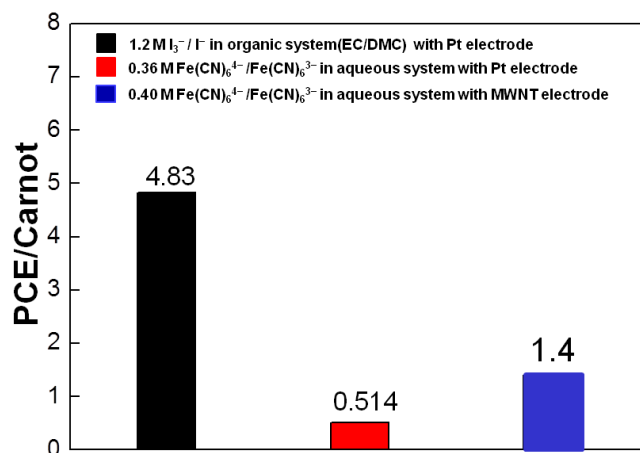
**Fig. 15. Thermal conductivity on DEC 0.5M, DEC 1M, DMC 0.5M at changing temperatures**

#### 4.4 Thermal conductivity

Thermal conductivity is directly concerned with PCE and temperature gradient. Electrolyte systems have to have low thermal conductivity in TG cell. To maintain temperature difference of each side (hot, cold), low thermal conductivity must be guaranteed. Thermal conductivity is indicated of 0.5 M concentration in EC/DEC and EC/DMC in figure 15. Thermal conductivities of all samples decrease as the temperature decrease.

Thermal conductivity of  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  in aqueous systems is from 0.55 to 0.65 W/m·K., and it in-

creases as the temperature rises. At high concentration, thermal conductivity increases due to the increment of charge species which carry thermal energies from one to another side.



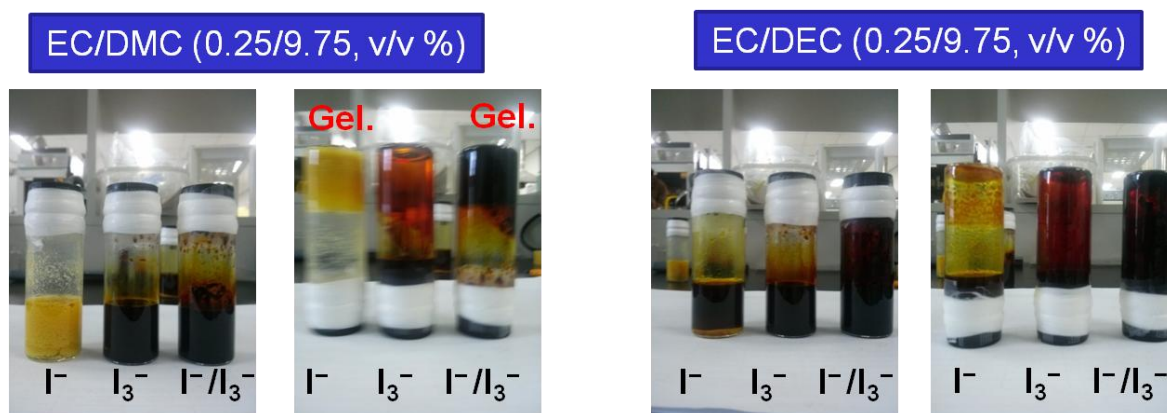
**Fig. 16. Comparisons of PCE/Carnot on I<sub>3</sub><sup>-</sup>/I<sup>-</sup> organic solution with Pt electrode and Fe(CN)<sub>6</sub><sup>4-</sup>**

**/Fe(CN)<sub>6</sub><sup>3-</sup> aqueous solution with Pt and MWNT electrodes**

4.6 Comparison on iodide based organic solution with Pt electrode and Fe(CN)<sub>6</sub><sup>4-</sup>/Fe(CN)<sub>6</sub><sup>3-</sup> aqueous solution with MWNT electrode.

TG cell efficiency is largely improved by utilizing carbon multiwalled nanotube (MWNT) electrode which has low electrical and thermal resistance. The PCE with MWNT electrodes / Carnot efficiency is shown to be 1.4 % in the literature, which is the highest one in the current field of TG cell. As shown in figure 16, we found 4.83 % of PCE/ Carnot efficiency at 1.2 M I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple in EC/DMC (0.25/9.75, v/v).

#### 4.7. Interaction between a linear carbonate and iodide.



**Fig. 17. Vial inversion experiments on 1.2 M  $I_3^-$  and  $I^-$  in EC/DMC (left), EC/ DEC (right)**

**(0.25/9.75. v/v)**

The vial inversion experiments were conducted to check an interaction of linear carbonate and ions in electrolyte after two days in 60 °C oven. The iodide has more structuring ability than the triiodide with linear carbonate as shown in figure 17 (left). The DMC can easily form a structure with iodide rather than DEC.

The viscosity and ionic conductivity measurements of diverse temperatures were conducted to verify the interaction between linear carbonate and iodide as shown in figure 18 and 19. In general, the ionic conductivity increases in case of high temperature due to reduced resistance of the electrolyte, and the viscosity decreases due to enhanced kinetic energy of a molecular. However, the ionic conductivity of EC/DMC system was reduced as the temperature increases from 50 to 60°C, and the viscosity greatly increases at 60 °C. We analogize this result may come from the structure made with linear carbonate and iodide in EC/DMC organic TG

cell systems. The structure formation between the DMC and iodide can be occur at hot side (60 °C). Meanwhile, the DMC cannot make the formations with the triiodide. We predict that this phenomenon induces the large OCV from activity changes of iodide and triiodide in the Nernst equation.

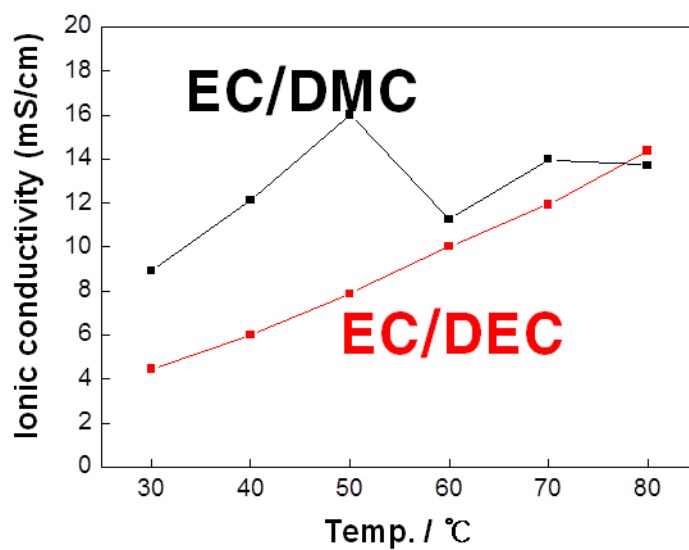


Fig. 18. Ionic conductivity on 1.2 M  $I_3^-/I^-$  redox couple in EC/DMC, EC/ DEC (0.25/9.75, v/v)

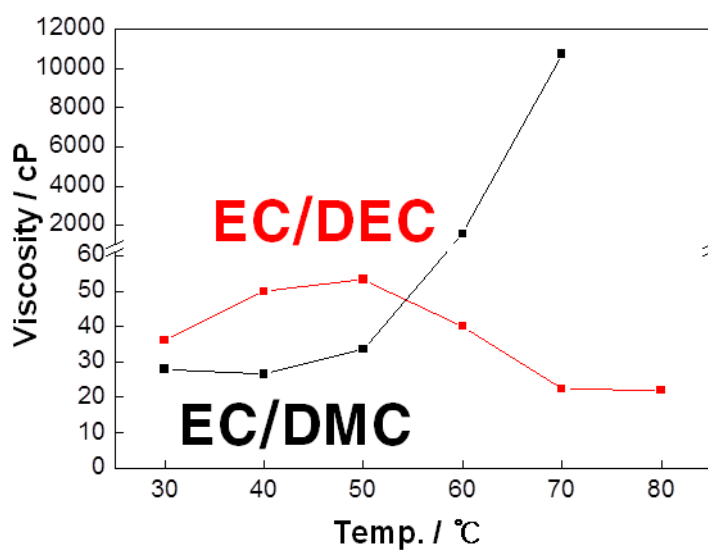


Fig. 19. Viscosity on 1.2 M  $I_3^-/I^-$  redox couple in EC/DMC, EC/ DEC (0.25/9.75, v/v)

## V. Conclusion

In this study, we checked the tendency of data on results by means of changing concentration and temperature gradient on  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox couple in aqueous solution. By increasing concentration, the short circuit currents increase from 300 to 1600  $\mu\text{A}$ . PCE increases as temperature gradient gets higher. The open circuit potential is clearly proportional to temperature gradient, and the trend of output power is also similar with them. The electrolyte resistance decreases by increasing concentrations, and thereby SCC increases. To find out the maximum values of power conversion efficiency(PCE), Seebeck coefficient (SC) and Output power, we utilize numerous concentrations of  $\text{I}_3^-/\text{I}^-$  redox couple by mixing various volume ratios of solvents such as EC, DEC, EMC and DMC. 1.2 M  $\text{I}_3^-/\text{I}^-$  redox couple in EC/DMC (0.25/9.75. v/v) was the best condition to get maximum value of PCE. SC values in EC/DMC systems is higher as compared with EC/DEC and EC/EMC. When temperature difference increases by using heating tape and water circulator, SC and PCE were also elevated, and the increment of SCC might be due to the decrement of internal resistance.

We analogize this result may come from the structure made with linear carbonate and iodide in EC/DMC organic TG cell systems. The structure formation between the DMC and iodide can be occur at hot side (60 °C). Meanwhile, the DMC cannot make the structure with the triiodide. We predict that this phenomenon induces the large OCV from activity changes of iodide and triiodide in the Nernst equation.



The PCE with MWNT electrodes / Carnot efficiency is shown to be 1.4 % in the literature, which is the highest one in the current field of TG cell. In our study, we found 4.83 % of PCE/ Carnot efficiency at 1.2 M  $I_3^-/I^-$  redox couple in EC/DMC (0.25/9.75, v/v).

We investigated the platinum electrode in  $I_3^-/I^-$  redox couple in organic solutions. The cost of platinum electrode is expensive as compared with others materials, although it has higher charge transfer reaction on the interface between electrode and interface. It has to be replaced to other materials with regard to cost competition. Nowadays, there are many promising electrode materials such as activated carbon, conductive polymer, and sulfate system electrode. Thus, we could achieve strong cost competition by changing the electrodes from platinum to others.

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## 요 약 문

### 카보네이트계 전해액/요오드 레독스 반응 기반 고효율

### 열전기화학전지

전 세계적으로, 전기와 화석 연료의 수요가 증가 하고 있다. 수요가 증가 함에 따라 가격 또한 증가 하고 있으므로 이에 대한 대체 에너지가 절실히 필요하다. 태양열, 지열, 공장 공정, 발전기 등 많은 곳에서 만들어진 열 에너지가 사용되지 못하고 그대로 버려지고 있다. 버려진 열을 우리가 사용할 수 있는 에너지로 바꿀 수 있다면, 많은 에너지를 절약 할 수 있다. 열전소자로서 현재까지 thermo-electric device 가 많이 연구 되어 왔다. 그러나 여러 디바이스적 한계에 부딪혀 있다.

열 전기화학전지는 동일한 전극을 양쪽 전극으로 사용하여, 각 전극부분에 온도차이를 주었을 때 전기에너지를 얻을 수 있는 장치이다. 이 전지는 열전소자와 달리 전하를 전달하는 매개체가 전해액의 이온 이며 상대적으로 높은 Seebeck 값을 나타낸다.

현재 열전기화학전지 연구는 수계 용액에 페리/페로시아나이드 산화-환원 커플을 이용한 전해액 바탕으로 효율을 올리고 가격 경쟁력을 증가 시키기 위하여 카본 바탕의 전극으로 대체되고 있는 추세 이다.

이번 연구에서 카보네이트 계 용액에 요오드 산화-환원 커플을 이용하여 열 전기화학전지 실험을 하였다. 카보네이트 계 용액의 경우 이차전지 분야에서 활발이 사용되고 있고, 요오드 산화-환원 커플은 DSSC 분야에서 사용 되고 있다.

카보네이트 계 용액을 다양한 조성에서 위 산화-환원 커플을 넣어 그 조성에 따라 효율이 어떻게 달라지는지 연구 하였다. 또한 요오드 산화-환원 커플의 농도에 따라 효율 변화도 확인 하였다.

현재 열 전기화학전지중 가장 큰 효율 값을 보이는 것은 수계 용액에서 MWNT 전극을 이용한 시스템이며, 카르노 효율 대비 power conversion efficiency 값이 1.4 % 이다. 카보네이트 계 용액에 요오드 산화-환원 커플을 이용하여 4.83 %까지 위 값을 증가 시켰다.

핵심어: 열화학전지, 지벡값, 효율, 카보네이트계 용액, 아이오딘