Thermal power generation during heat cycle near room temperature

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We demonstrate that a sodium-ion secondary battery (SIB)-type thermocell consisting of two types of Prussian blue analogue (PBA) with different electrochemical thermoelectric coefficients ($S_{EC} = \partial V/\partial T$; $V$ and $T$ are the redox potential and temperature, respectively) produces electrical energy during heat cycles. The device produces an electrical energy of 2.3 mVeV/PB per heat cycle between 295 K ($= T_1$) and 323 K ($= T_2$). The ideal thermal efficiency ($\eta_i = 1.0\%$), which is evaluated using the heat capacity ($C = 4.16$ mJ/K) of ideal Na$_2$Co[Fe(CN)$_6$], reaches 11% of the Carnot efficiency ($\eta_{CB} = 8.7\%$). Our SIB-type thermocell is a promising thermoelectric device that harvests waste heat near room temperature.

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The thermoelectric device, which can convert heat into electricity and vice versa, is a fascinating technology for a smart society. In the development of thermoelectric semiconductors, the Seebeck coefficient [$S \equiv \Delta V/\Delta T$, where $\Delta V$ ($\Delta T$) is the voltage (temperature) difference between the hot and cold electrodes] is a significant material parameter. $\beta_1$Te$_3$ ($S = 0.2$ mV/K) at room temperature and PbTe ($= 0.12$ mV/K) at 300 K are prototypical semiconductors and exhibit high dimensionless figures of merit ($ZT \equiv S^2/\rho T$, where $T$, $\rho$, and $\kappa$ represent the temperature, resistivity, and thermal conductivity, respectively). Moreover, they have practical use for Peltier cooling and power generation in space vehicles. These devices, however, require a high-grade heat source of several hundred Kelvins to achieve a thermal efficiency of ~10%. On the other hand, several thermocells, which consist of hot and cold electrodes of identical type and solvable redox couples, were proposed in the 1950s and 1960s. The thermocell converts $\Delta T$ into $\Delta V$ between the electrodes through the electrochemical thermoelectric coefficient ($S_{EC} \equiv \partial V/\partial T$, where $V$ and $T$ are the redox potential and temperature, respectively). For example, a thermocell using [Fe(CN)$_6$]$^{3+}$/[Fe(CN)$_6$]$^{4+}$ was demonstrated to convert $\Delta T$ into $\Delta V$ between the two electrodes. The thermocell, however, needs a pump to transfer the accumulated species from the electrode region, which results in the loss of a major advantage, the absence of moving parts. Kobayashi et al. proposed a sodium-ion secondary battery (SIB)-type thermocell, whose configuration is the same as that of a SIB, except that the anode and cathode materials are the same. They fabricated a CR2032-type thermocell made of layered oxides, for example, NaxCoO$_2$ and Na$_{0.5}$MnO$_2$, and confirmed that $\Delta V$ changes linearly with $\Delta T$. Compared to the aforementioned thermocell, the SIB-type thermocell utilizes the $S_{EC}$ value of a redoxable solid, and hence has no moving parts.

If the thermocell is made of two types of redox material with different $S_{EC}$, the heating/cooling of the thermocell changes the cell voltage ($V_{cell}$) between the anode and cathode. In other words, such a thermocell produces electrical energy during heat cycles, in sharp contrast with the thermoelectric devices described above. Lee et al. and Yang et al. demonstrated that this idea is feasible using solvable redox couples, for example, [Fe(CN)$_6$]$^{3+}$/[Fe(CN)$_6$]$^{4+}$ and Cu$^2$/Cu$^+$, as the anode and Prussian blue analogues (PBAs) as the cathode. These thermocells, however, are bulky and heavy because the electrolyte contains redoxable ions. To overcome this drawback, we propose a SIB-type thermocell that consists of two types of redoxable solid with different $S_{EC}$. It is possible to minimize the amount of electrolyte used in this thermocell. This type of thermocell extends the use of so-called battery materials from energy storage to energy conversion.

PBAs, whose chemical formulas are Li$_x$M[Fe(CN)$_6$], and Na$_y$M[Fe(CN)$_6$], whose $M$ is a transition metal, are promising candidates for use as the cathode materials in lithium ion batteries and SIBs. For example, a thin film of Li$_{1.6}$Co[Fe(CN)$_6$]$\cdot$2.5H$_2$O shows a high capacity of 132 mAh/g with good cyclability. PBAs have face-centered cubic structure ($Fm\overline{3}m$, $Z = 4$). They consist of a three-dimensional (3D) jungle-gym-type host framework and guest Li$^+$ ions, which are accommodated in the nanopores of the framework. Importantly, the host framework, Fe–CN–M–NC–Fe, is robust against Li$^+$/Na$^+$ deintercalation and concomitant oxidation of M and Fe. In fact, the host framework of Li$_{1.4}$Co[Fe(CN)$_6$]$\cdot$2.5H$_2$O is stable even if we remove all of the Li$^+$ from the framework. Recently, Magnússon et al. systematically investigated the $S_{EC}$ value of Li$_{y}$Co[Fe(CN)$_6$]$_x$ for various $x$ and $y$.

In this study, we fabricated a SIB-type thermocell with a thin film of Na$_x$Co[Fe(CN)$_6$]$\cdot$3.6H$_2$O (NCF71) as the anode and a thin film of Na$_x$Co[Fe(CN)$_6$]$\cdot$2.9H$_2$O (NCF90) as the cathode. The $S_{EC}$ values are 0.53 and 1.32 mV/K for NCF71 at $x = 0.51$ and NCF90 at $x = 0.71$, respectively. Owing to the difference in $S_{EC}$, the device produces an electrical energy of 2.3 mVeV/NCF90 per heat cycle between 295 K ($= T_1$) and 323 K ($= T_2$). The ideal thermal efficiency ($\eta_i = 1.0\%$) reaches 11% of the Carnot efficiency ($\eta_{CB} = 8.7\%$). The NCF71 and NCF90 films were synthesized by means of electrochemical deposition on indium tin oxide transparent electrodes. Details of the synthesis conditions are described in the literature. The chemical compositions of the films were determined by the inductively coupled plasma method.
and CHN organic elemental analysis (PerkinElmer 2400 CHN Elemental Analyzer). Both the compounds show face-centered cubic structure (Fm$ar{3}$m; Z = 4) with lattice constants (a) of 10.3 Å (NCF71) and 10.4 Å (NCF90). The film thickness is ≈1.0 μm, as determined by a profilometer (Ulvac DEKTAK3030). The typical area of a film is 1.0 cm$^2$. The mass of each film was evaluated from the thickness, area, and ideal density.

Figures 1(a) and 1(b) show the charge and discharge curves of the NCF71 and NCF90 films, respectively, in an aqueous solution of 10 mol/L NaClO$_4$. The electrochemical properties of the films were investigated using a potentiostat (HOKUTO DENKO HJ1001SD8) with a beaker-type cell in the three-pole configuration. The working, reference, and counter electrodes were the PBA electrode, and Pt, respectively. In NCF71 [Fig. 1(a)], the discharge curve shows a single plateau (plateau I) at ≈0.55 V versus Ag/AgCl electrode, and Pt, respectively. In NCF90 [Fig. 1(b)], the discharge curve shows a single plateau (plateau I) at ≈0.55 V versus Ag/AgCl, which is to the reduction reaction$^{24}$ $\text{Na}_0.6\text{Co}_3^+\text{[Fe}^{2+}\text{(CN)}_6\text{]}_0.9 + 0.71\text{Na}^+ \rightarrow \text{Na}_0.8\text{Co}^{2+}\text{[Fe}^{2+}\text{(CN)}_6\text{]}_0.71$. The discharge capacity is 68 mAh/g, which is close to the ideal value (= 72 mAh/g). In the discharge process, Na$^+$ is inserted into the framework, which causes the reduction of Fe$^{3+}$ to maintain charge neutrality. In NCF90 [Fig. 1(b)], the discharge curve shows two plateaus (plateaus II and III) at ≈1.0 and ≈0.53 V. Plateau II (x ≤ 0.6) at ≈1.0 V is ascribed to the reaction$^{16}$ $\text{Co}^{3+}[\text{Fe}^{6+}\text{(CN)}_6\text{]}_0.9 + 0.6\text{Na}^+ \rightarrow \text{Na}_0.6\text{Co}^{2+}[\text{Fe}^{2+}\text{(CN)}_6\text{]}_0.9$. Plateau III (x ≥ 0.6) at ≈0.53 V is ascribed to the reaction$^{16,25}$ $\text{Na}_0.6\text{Co}^{2+}[\text{Fe}^{2+}\text{(CN)}_6\text{]}_0.9 + \text{Na}^+ \rightarrow \text{Na}_1\text{Co}^{3+}[\text{Fe}^{2+}\text{(CN)}_6\text{]}_0.9$. The discharge capacity is 115 mAh/g, which is close to the ideal value (= 132 mAh/g). We use plateau I of the NCF71 film and plateau III of the NCF90 film in the SIB-type thermocell because their redox potentials are almost the same.

To determine the $S_{EC}$ values of the NCF71 (plateau I) and NCF90 (plateau III; x ≥ 0.6) films, we fabricated a specially designed two-pole cell whose anode (T$_{anode}$) and cathode (T$_{cathode}$) temperatures are independently controlled by Peltier elements. The cathode, anode, and electrolyte were the thin film, Na metal, and propylene carbonate containing 1 mol/L NaClO$_4$, respectively. We carefully measured V against T$_{cathode}$ with T$_{anode}$ fixed at 295.3 K. Figures 2(a) and 2(b) show the V values of NCF71 at x = 0.51 at plateau I and of NCF90 at x = 0.71 at plateau III, respectively, against T$_{cathode}$. We evaluated $S_{EC}$ by least-squares fittings with primary functions, as indicated by the solid straight lines.

Thus, the $S_{EC}$ values are determined to be 0.53 and 1.32 mV/K for NCF71 at x = 0.51 (plateau I) and NCF90 at x = 0.71 (plateau III), respectively. The difference (= 0.79 mV/K) in $S_{EC}$ between NCF71 and NCF90 is significant.

We fabricate a SIB-type thermocell (two-pole beaker-type cell) whose anode, cathode and electrolyte are the as-grown NCF71 film, a pre-oxidized NCF90 film, and an aqueous solution of 10 mol/L NaClO$_4$, respectively (inset of Fig. 3). The NCF90 film was pre-oxidized at $V_{upper}$ = 0.65 V against Ag/AgCl in an aqueous solution of 10 mol/L NaClO$_4$. Here, we define $T_{L}$ (= 295 K) and $T_{H}$ (= 323 K) as the lowest and highest temperatures, respectively. The as-prepared device, which showed a finite $V_{cell}$ (= 0.19 V), was discharged to 0 V under a constant current condition (I = 2.9 μA). Then, we slowly increased the temperature (T) of the device from $T_L$ to $T_H$. Figure 3(a) shows $V_{cell}$ against T in this heating process. As expected, $V_{cell}$ increases linearly with T at a rate of 0.96 mV/K. The increase in $V_{cell}$ is reasonably ascribed to the difference in $S_{EC}$ between the anode and cathode. Moreover, the observed value (= 0.96 mV) is close to the difference (≈ 0.79 mV) in $S_{EC}$ between NCF71 and NCF90. At $T_H$, the device shows a finite $V_{cell}$ (= 26 mV). Figure 3(b) shows the first discharge process at $T_H$ at I = 2.9 μA. $V_{cell}$ decreases linearly to 0 V in proportion to the moved charge. The final moved charge is 0.09 e per NCF90 unit. The electric work done in this discharge process was 1.2 meV/NCF90.

The heat cycle of the SIB-type thermocell consists of four processes, as shown schematically in Fig. 4. (i) heating from...
respectively) of the SIB-type thermocell. The output work (\(W\)) and second heat cycles. The lowest (\(T_h\)) of the heat cycle consists of four processes: (i) heating from \(T_i\) to \(T_H\), (ii) discharge at \(T_L\), (iii) cooling from \(T_H\) to \(T_L\), and (iv) discharge at \(T_L\). The heating and cooling processes are performed without current (\(I = 0\)).

\[ T_i \rightarrow T_H, \text{ (ii) discharge at } T_H, \text{ (iii) cooling from } T_H \text{ to } T_L, \text{ and (iv) discharge at } T_L. \]

Figures 5(a) and 5(b) show the variation of \(V_{cell}\) and current \((I)\) in the SIB-type thermocell against time in the first and second heat cycles. The lowest \((T_H)\) and highest \((T_L)\) temperatures are 295 and 323 K, respectively. The discharge processes were performed under a constant current condition \((I = 2.9 \mu A)\).

In conclusion, we demonstrate that a SIB-type thermocell consisting of two types of PBA with different \(S_{EC}\) values can harvest waste heat near room temperature. The device produces an electrical energy of 2.3 meV/NCF90 per heat cycle between 295 and 323 K. The ideal thermal efficiency \((\eta = 1.0\%\) reaches 11\% of the Carnot efficiency \((\eta_{th} = 8.7\%\)). We emphasize that our SIB-type thermocell can be easily formed into a sheet or a large device at a low cost, because it has the same device structure as SIBs.

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1. D. A. Wright, Nature 181, 834 (1958).
2. J. P. Heremans, V. Jovicic, E. S. Toberer, A. Saramat, K. Kuroasaki, A. Charoenphakdee, S. Yamakata, and G. J. Snyder, Science 321, 554 (2008).
3. H. J. Goldsmid, Introduction to Thermoelectricity (Springer, Berlin, 2010).
4. C. B. Vining, Nat. Mater. 8, 83 (2009).
5. T. Ikeshoji, Bull. Chem. Soc. Jpn. 60, 1505 (1987).
6. W. Kobayashi, A. Kinoshita, and Y. Moritomo, Appl. Phys. Lett. 107, 073906 (2015).
7. S. W. Lee, Y. Yang, H.-W. Lee, H. Ghasemi, D. Kraemer, G. Chen, and Y. Cui, Nat. Commun. 5, 3942 (2014).
8. Y. Yang, S. W. Lee, H.-W. Lee, H. Ghasemi, J. Loonis, D. Kraemer, G. Zheng, Y. Cui, and G. Chen, Proc. Natl. Acad. Sci. U.S.A. 111, 17011 (2014).
9. I. Quickenden and Y. Mua, J. Electrochem. Soc. 142, 3985 (1995).
10. T. Matsuda and Y. Moritomo, Appl. Phys. Express 4, 047101 (2011).
11. Y. Moritomo, M. Takachi, Y. Kurihara, and T. Matsuda, Appl. Phys. Express 5, 041801 (2012).
12. M. Takachi, T. Matsuda, and Y. Moritomo, Jpn. J. Appl. Phys. 52, 044301 (2013).
13. T. Matsuda, M. Takachi, and Y. Moritomo, Chem. Commun. 49, 2750 (2013).
14. Y. Lu, L. Wang, J. Cheng, and J. B. Goodenough, Chem. Commun. 48, 6544 (2012).
15. M. Takachi, T. Matsuda, and Y. Moritomo, Appl. Phys. Express 6, 025802 (2013).
16. M. Takachi, T. Matsuda, and Y. Moritomo, Jpn. J. Appl. Phys. 52, 092020 (2013).
17. D. Yang, J. Xu, X.-Z. Liao, Y.-S. He, H. Liu, and Z.-F. Ma, Chem. Commun. 50, 13377 (2014).
18. H. W. Lee, R. Y. Wang, M. Pasta, S. W. Lee, N. Liu, and Y. Chi, Nat. Commun. 5, 5280 (2014).
19. L. Wang, J. Song, R. Qiao, L. A. Wray, M. A. Hossain, Y. D. Chung, W. Yang, Y. Lu, D. Evans, J.-J. Lee, S. Vaii, A. Ahaoo, M. Nishijima, S. Kakimoto, and J. B. Torrance, J. Am. Chem. Soc. 137, 2548 (2015).
20. S. Yu, Y. Li, Y. Lu, B. Xu, Q. Wang, M. Yan, and Y. A. Jing, J. Power Sources 275, 45 (2015).
21. Y. You, X. L. Wu, Y. X. Yin, and Y. G. Guo, Energy Environ. Sci. 7, 1643 (2014).
22. R. L. Magnússon, W. Kobayashi, M. Takachi, and Y. Moritomo, AIP Adv. 7, 045002 (2017).
23. Note that the \(S_{EC}\) values reported in Ref. 22 is the difference between cathode (PBA) and anode (Li) material.
24. F. Nakada, H. Kamioka, Y. Moritomo, J. E. Kim, and M. Takata, Phys. Rev. B 77, 224436 (2008).
25. K. Igarashi, F. Nakada, and Y. Moritomo, Phys. Rev. B 78, 235106 (2008).