Development of battery-type thermocell

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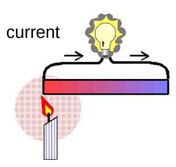
Introduction

- Recovery of waste heat with low temperature (T<200 ˚C) is highly desired.
- Semiconductor thermoelectric materials are expensive and need high-T waste heat for the high-performance thermoelectric conversion.
- Electrochemical thermoelectric effect has been studied, and a large value (~1 mV/K) of $\Delta V/\Delta T$ was observed. However, it needs expensive Pt electrodes.
- The replacement of the Pt electrode by other cheap electrode is expected.

Summary

We have fabricated a battery-type thermocell and demonstrated the electrochemical thermoelectric effect in the thermocell.
(1) A large value of $\Delta V/\Delta T$ (ΔV: thermoelectric voltage, ΔT: temperature difference) of -0.720 mV/K was observed for P2-type $Na_{1/2}CoO_2$.
(2) Time (t) evolution of ΔV was qualitatively explained by mean-field theory of chemical potential (Φ).

Semiconductor thermoelectrics



$\Delta V = S\Delta T$

ΔV : voltage, S : Seebeck coefficient, ΔT : temperature difference

~70 % of total energy is abandoned as waste heat→waste heat recovery

Dimensionless-figure-of-merit

$$ZT = \frac{S^2}{\rho\kappa}T$$

ρ : resistivity
κ : thermal conductivity
T : temperature

Maximum efficiency

$$\eta_{max} = \frac{T_H - T_L}{T_H}\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_L/T_H}$$

T_H: T at hot side, T_L: T at cold side

T_H=1000 K, T_L=500 K, ZT=1 → η=10.8%

~0.2 mV/K for Bi_2Te_3

Electrochemical thermoelectric effect

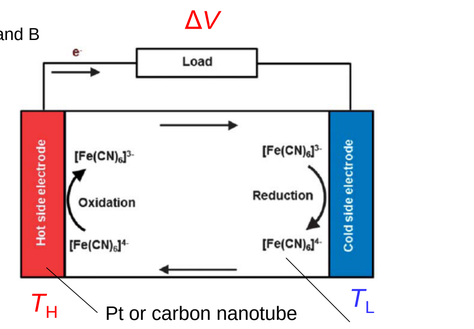
Redox reaction of chemical species A and B

oxidation
$A + ne^- \leftrightarrows B$
reduction

Difference of Gibbs free energies between A and B under ΔT

$$\Delta V = -\frac{\Delta G}{en}$$

Electron charge
Number of reacted electrons



$[Fe(CN)_6]^{3-} + e^- \leftrightarrow [Fe(CN)_6]^{4-}$

T. I. Quickenden and Y. Mua, J. Electrochem. Soc. 142, 3985 (1995).

R. Hu *et al.*, Nano Lett. 10, 838 (2010).

$\Delta V/\Delta T$ ~ 1 mV/ K, ~ 1 % of Carnot efficiency, 0.2 - 0.3 W/m^2 (@ RT with ΔT ~ 30-50 K)

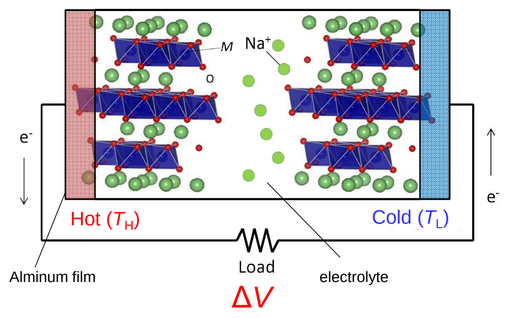
Pt electrode is expensive so that we want to replace it by cathode of ion secondary battery.

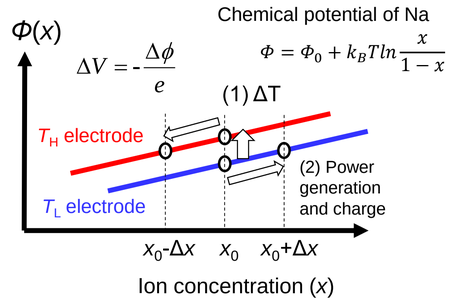
Collaboration between experiments and computational science on thermoelectric effect in a battery-type thermocell

Thermoelectrics + **Ion secondary battery**

→ battery-type thermocell

Calculation of voltage (V) at various temperature (T) and ion concentration (x) is essential to realize a large $\Delta V/\Delta T$ value!





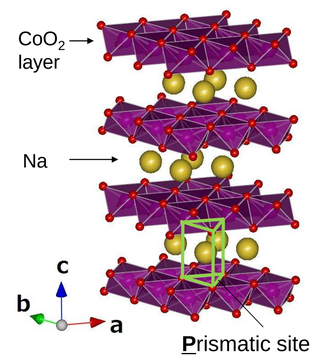
characteristics
(1) Electricity converted from heat can be stored as chemical energy (charged by temperature difference (ΔT), discharged by releasing ΔT)
(2) Easy to fabricate, low price

$\Delta V/\Delta T$= - 0.720 mV/K for $Na_{0.5}CoO_2$

W. Kobayashi, A. Kinoshita, and Y. Moritomo, Appl. Phys. Lett. 107, 073906 (2015).

Crystal structure

P2-type $Na_{2/3}CoO_2$

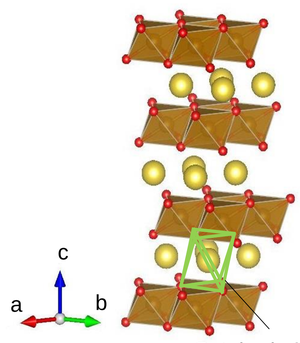


Prismatic site

- space group: $P6_3/mmc$
- atomic positions: 2a Co(0, 0, 0), 4f O(1/3, 2/3, z), 2b Na1(0, 0, 1/2), 2d Na2(1/3, 1/3, 3/4)
- a=2.82748(4) Å, c=10.9319(2) Å, z=0.0858(3) at 300 K
- occupancy of Na1 and Na2: g_1=0.234(3), g_2=0.356(3) at 300 K

D. Tanabe et al., Phys. Status Solidi RRL 7, 1097 (2013).

O3-type $NaCoO_2$



Octahedral site

- space group :R-3m
- atomic positions: 3a Na(0, 0, 0) , 3b Co(0, 0, 1/2), 6c O(0, 0, z)
- a=2.88629(2) Å, c=15.58698(11) Å, z=0.23017(9) at 300 K
- occupancy of Na: g=0.987(4) at 300 K

T. Shibata et al., Sci. Rep. 5, 9006 (2015).

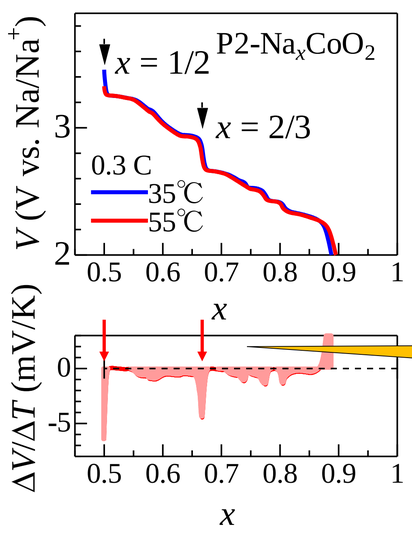
Results and Discussion

Y. Fukuzumi, W. Kobayashi, and Y. Moritomo, in preparation.

Experimental and theoretical studies on structure in P2- and O3-Na_xCoO_2 at various x were reported.
Experiments: Q. Huang et al., Phys. Rev. B70, 184110 (2004). [P2], R. Berthelot, D. Carlier and C. Delmas, Nat. Mater. 10, 74 (2011). [P2], L. Viciu et al., Phys. Rev. B73, 174104 (2006). [O3], Y. Lei et al., Chem. Mater. 26, 5288 (2014). [O3]
Theory: Y. Hinuma, Y. S. Meng, and G. Ceder, Phys. Rev. B77, 224111 (2008). [P2]

Evaluation of $\Delta V/\Delta T$

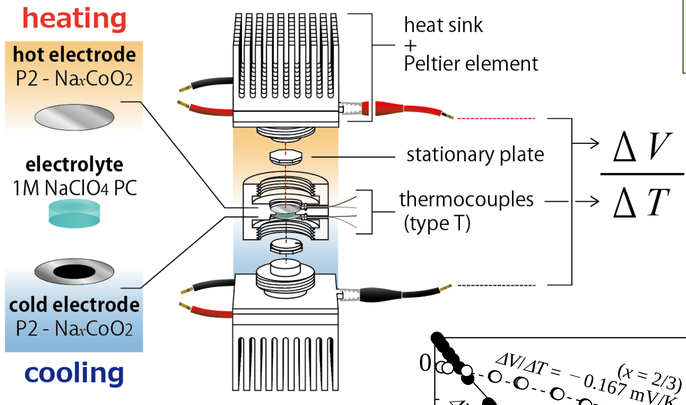
Discharge curve of P2-Na_xCoO_2 at 35 and 55 ˚C

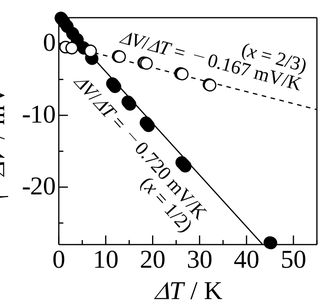


Large $\Delta V/\Delta T$ was observed at around x=1/2 and 2/3.

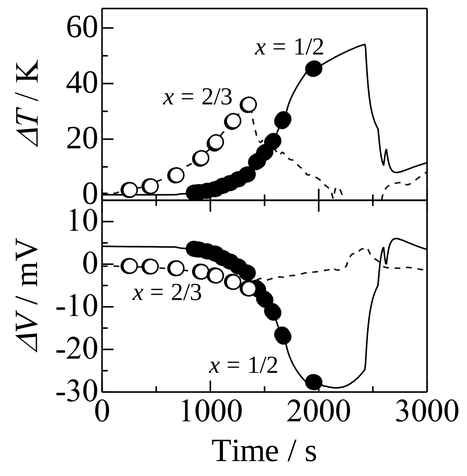
- 0.720 mV/K for x=1/2,
- 0.167 mV/K for x=2/3

Schematic figure of thermocell





ΔT and ΔV v.s. time



Objectives

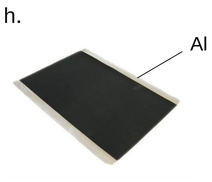
To realize a thermocell with high performance and low price, we investigated electrochemical thermoelectric effect of P2- and O3-type Na_xCoO_2.

Experiments

Preparation of paste-type electrode

O3-type : $Na_{0.99}CoO_2$
A mixture of Na_2O_2 and Co_3O_4 was twice calcined at 550 ˚C in oxygen for 24 h.
P2-type : $Na_{0.66}CoO_2$
A mixture of Na_2CO_3 and Co_3O_4 was calcined at 800 ˚C in air for 12 h.

Electrode preparation:
powders : acetylene black : polyvinylidenefluoride (PVDF) = 8 : 1 : 1
Dried at 373 K for 12h in vacuum



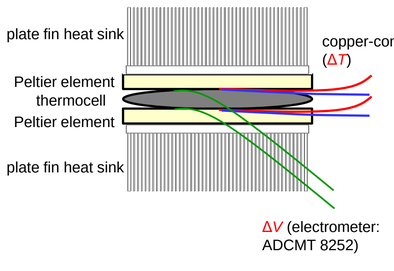
Discharge measurement

Galvanic beaker cell was used.
- Negative electrode : stainless steel with sodium metal
- Electrolyte : propylene carbonate (PC) containing 1 mol/l $NaClO_4$
- Charge/Discharge current : 12 μA
- Cut off voltage : 2.0 V - 3.4 V

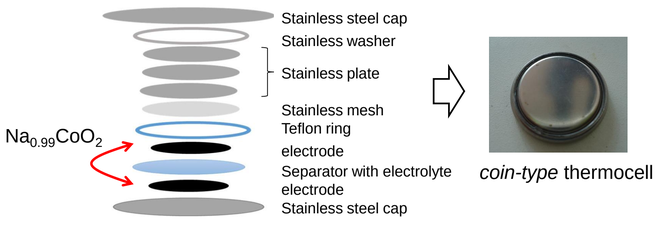
beaker cell

Thermoelectric property

- ΔV measurement : Electrometer (ADCMT 8252)
- ΔT measurement : nanovolt meter (Agilent 34420A) with copper-constantan thermocouples
- Application of ΔT : Source meter (Matsuzada P4K80) with commercially available Peltier element



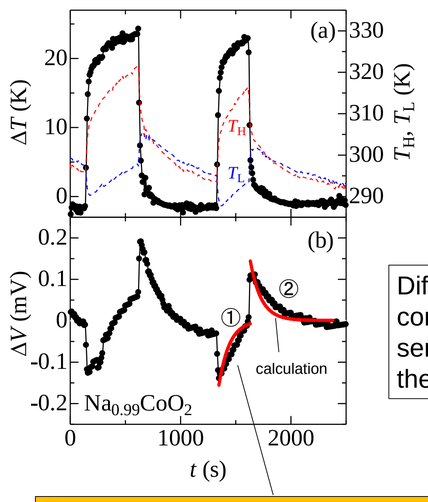
Preparation of a coin-type thermocell



coin-type thermocell

Electrolyte:
1mol/L $NaClO_4$ PC (Propylene Carbonate)

Time (t) dependence of ΔV in $Na_{0.99}CoO_2$



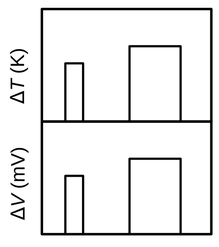
① Na ions move from hot to cold part.
② The Na ions return to the original electrode.

characteristics

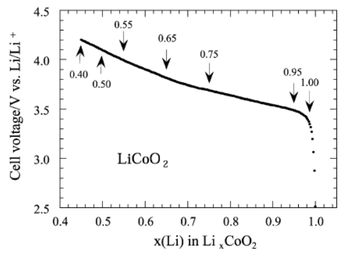
(1) Magnitude of ΔV decreases with t
(2) Sign of ΔV changes

Typical behavior of ΔV v.s. time in semiconductor thermoelectrics

Different from conventional semiconductor thermoelectrics



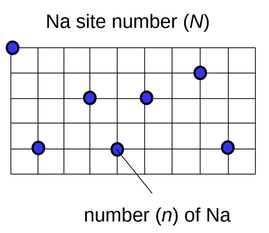
Discharge curve of Li_xCoO_2



Analysis of time dependence of ΔV

W. Kobayashi, A. Kinoshita, and Y. Moritomo, Appl. Phys. Lett. 107, 073906 (2015).

Chemical potential (Φ) as a function of x



Configuration number

$$W = \frac{N!}{n!(N-n)!} \Rightarrow S \Rightarrow G \Rightarrow \frac{\partial G}{\partial n} = \phi$$

$$\phi = \phi_0 + k_B T \ln\left(\frac{x}{1-x}\right)$$

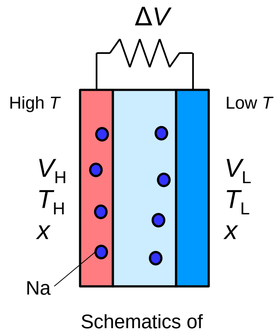
site potential

Difference between chemical potentials of Na in hot and cold electrodes

$$\Delta V = -\frac{\Delta\phi}{e}$$

Electron charge

ΔV with $\Delta T \neq 0$ at t=0



Schematics of thermocell

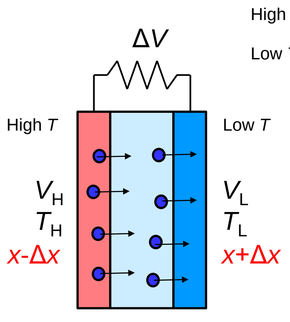
$$\Delta V = -\frac{k_B}{e}\Delta T \ln\left(\frac{x}{1-x}\right)$$

($\Delta T = T_H - T_L$, $\Delta V = V_H - V_L$)

$$\frac{\Delta V}{\Delta T} = -\frac{k_B}{e}\ln\left(\frac{x}{1-x}\right)$$

-395.2 μV/K at x=0.99

①ΔV with $\Delta T \neq 0$ at t>0



High T: $Na \rightarrow Na^+ + e^-$
Low T: $Na^+ + e^- \rightarrow Na$

Schematics of thermocell

Na amount transferred from hot part to cold part

$$\Delta x(t) = \frac{1}{mF}\int_0^t \frac{\Delta V(t)}{R}dt$$

Number of moles of $Na_{0.99}CoO_2$ (=8.78*10^{-6} mol)

Internal resistance (=600 Ω)

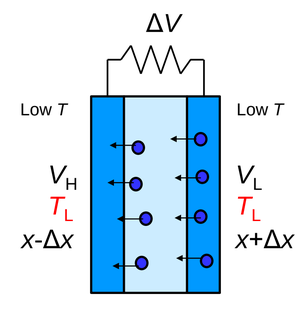
1st term > 2nd term

$$\Delta V(t) = -\frac{k_B}{e}\left\{T_H \ln\left(\frac{x-\Delta x(t)}{1-x+\Delta x(t)}\right) - T_L \ln\left(\frac{x+\Delta x(t)}{1-x-\Delta x(t)}\right)\right\}$$

Δx increases till $\Delta V \rightarrow 0$

Δx=0.0015

②ΔV with ΔT=0 at t>0



Schematics of thermocell

1st term < 2nd term

$$\Delta V(t) = -\frac{k_B}{e}\left\{T_L \ln\left(\frac{x-\Delta x(t)}{1-x+\Delta x(t)}\right) - T_L \ln\left(\frac{x+\Delta x(t)}{1-x-\Delta x(t)}\right)\right\}$$

Sign of ΔV changes from negative to positive → $\Delta x \rightarrow 0$, $\Delta V \rightarrow 0$