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To the press and whom it may concern,

University of Tsukuba  
National Institute of Technology, Gunma College  
Focus Systems Corporation

**Tertiary Batteries Utilizing Phase Change Material Successfully Achieve Higher Voltage  
— Toward Realizing Independent Power Supplies  
Charged in a Thermal Environment Near Room Temperature —**

Key points of research results

1. We successfully raised the battery voltage of a tertiary battery to approx. 120 mV using phase change material (PCM) for the electrode.
2. The tertiary battery shows promise as a power source for various sensors and other devices without the need for replacement or (maintenance) management.
3. Further increases in electromotive force (EMF) are anticipated depending on future material design.

The research group, led by Professor Yutaka Moritomo from Tsukuba Research Center for Energy Materials Sciences (TREMS), Faculty of Pure and Applied Sciences, University of Tsukuba, and Assistant Professor Takayuki Shibata from National Institute of Technology, Gunma College, prototyped beaker cell-type tertiary batteries<sup>\*1</sup> with cobalt Prussian blue analogues<sup>\*2</sup> exhibiting phase transition, and successfully generated an electromotive force of approximately 120 mV by raising the temperature from 13°C to 47°C. The thermal efficiency<sup>\*3</sup> of the tertiary batteries is 0.9%, equivalent to 11% of the theoretical efficiency.<sup>\*4</sup>

With the goal of realizing Society 5.0, a future society where IoT and other technologies are expected to be widely utilized, the global market for sensors is predicted to reach one trillion units by 2023. It would be impractical, however, to replace or manage the batteries of such a large number of sensors. Tertiary batteries are self-distributed power sources<sup>\*5</sup> that can be charged by ambient heat near room temperature—which is freely available from the surrounding environment—without the need for replacement or management. In light of this, the tertiary battery is considered to be one of the technologies essential for Society 5.0. The research group has long proposed the tertiary battery as a future self-distributed power source.

The group has been performing R&D based on the assumption that “since the redox potential of a substance changes discontinuously before and after a phase transition, the use of phase change material for the electrode should increase the electromotive force of the tertiary battery.” The use of cobalt Prussian blue analogues exhibiting phase transition resulted in an electromotive force of approximately 120 mV being obtained from the tertiary batteries with a temperature increase from 13°C to 47°C.

Future design and development of phase change material are expected to further increase the electromotive force. This industry-academia collaborative R&D will continue to be advanced with a view to societal implementation of tertiary batteries.

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## Research background

A “tertiary battery” is a self-distributed power source that is charged by ubiquitous environmental heat near room temperature. It is an “independent” power supply that converts temperature changes of several tens of degrees near room temperature—which are ubiquitous on earth—into electricity. These changes include day and night temperature variations; sunny and shadow areas; putting on and removing clothes or entering and exiting a room; and when an air-conditioner is running and when it is not. The tertiary battery also has “dispersibility” in the sense that it can be installed anywhere. With the goal of realizing the potential of the Internet of Things (IoT), the sensors market is predicted to reach one trillion units annually by 2023. It would be impractical to replace or manage the batteries of such a large number of sensors. Moreover, sensors may be installed in deserts, oceans, dense forests, mountains and other hard-to-reach areas in quite a few cases. In this regard, self-distributed power sources have an advantage in that they need not be replaced or managed. Thus, the tertiary battery is considered to be one of the technologies essential for Society 5.0, a future society proposed by the Cabinet Office, the Government of Japan. For example, tertiary batteries used as the power source for security cameras installed in a building are charged when the air conditioner is turned on and off during the day and night, which allows the security cameras to continue to be permanently driven. As the power source for GPS sensors attached to baggage, tertiary batteries are charged as the temperature changes when the baggage is loaded and unloaded, which allows the baggage’s positional information to continue to be permanently transmitted.

The research group has prototyped beaker cell-type tertiary batteries using cobalt Prussian blue analogues (Co-PBA: Fig.1) thin films and manganese Prussian blue analogues (Mn-PBA) thin films as electrode materials, to demonstrate their device performance. However, the electromotive force obtained from a temperature change from 13°C to 47°C was as low as 39 mV, which made it impossible to drive a sensor with a single cell. Accordingly, research and development has been performed based on the assumption that “since the redox potential of a substance changes discontinuously before and after a phase transition, the use of a phase change material for the electrodes should increase the electromotive force of the tertiary battery.” (Fig. 2)

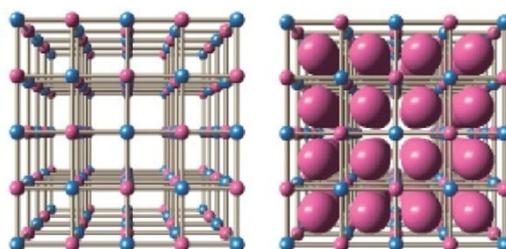


Fig. 1 Schematic crystal structures of cobalt Prussian blue analogues. The structure on the left shows a fully charged state, whereas the structure on the right shows a completely discharged state. Large red balls, small blue balls, and small red balls indicate sodium ions, cobalt ions, and iron ions, respectively.

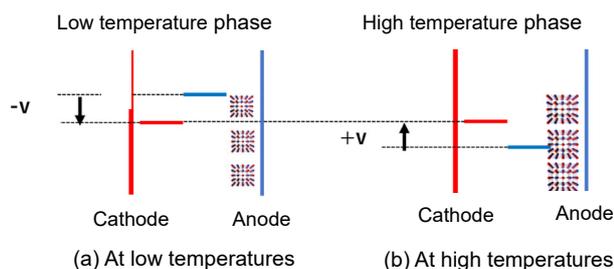


Fig. 2 Schematic illustration of tertiary batteries utilizing phase transition. In this example, the redox potential of the materials is assumed to be high in the low-temperature phase and low in the high-temperature phase.

## Research content and results

Thin films of two pairs of cobalt Prussian blue analogues ( $\text{Na}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.82}$  and  $\text{Na}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.90}$ ) were synthesized on an indium tin oxide (ITO) transparent electrode by the electrolytic deposition method. The film thickness was approximately 1  $\mu\text{m}$ .  $\text{Na}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.82}$  (NCF82) underwent a phase transition from a low-temperature phase to a high-temperature phase just above room temperature. On the other hand,  $\text{Na}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.90}$  (NCF90) remained in a low-temperature phase. The NCF90 and NCF82 thin films were previously oxidized to 1.01V against the Ag/AgCl standard electrode, and beaker-cell-type tertiary batteries were assembled. The cathode, anode, and electrolyte were NCF90, NCF82 and 10mol/L  $\text{NaClO}_4$  aqueous solution, respectively. By raising the temperature from 13°C to 47°C in the batteries, an electromotive force of approximately 120 mV was successfully generated (Fig. 3 (a)). Also, when the batteries were discharged at 47°C, a charge amount of 2.3 mAh/g was extracted (Fig. 3 (b)). The thermal efficiency was estimated to be 0.9%, taking into consideration the specific heat and latent heat of Co-PBA. This efficiency is equivalent to 11% of the theoretical efficiency.

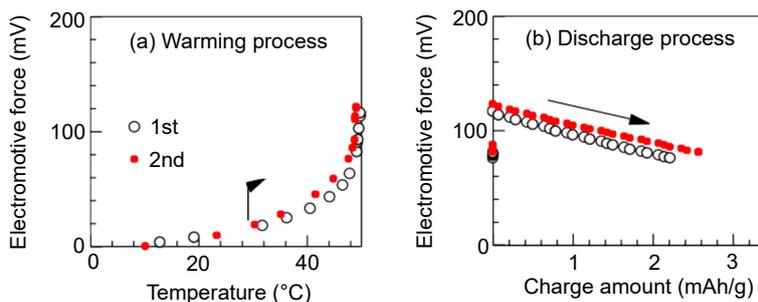


Fig. 3 (a) Warming process and (b) Discharge process of tertiary batteries utilizing phase transition. Open circles and red circles indicate the first and second data respectively. The lower limit voltage of the discharge process is set to 80 mV.

## Future developments

A tertiary battery utilizing phase transition is a promising technology to obtain a large amount of electromotive force from ubiquitous environmental heat. Future design and development of phase change material are expected to further increase the electromotive force. This industry-academia collaborative R&D will continue to be advanced with a view to societal implementation of tertiary batteries.

## Glossary

- \* 1 Tertiary battery  
A tertiary battery is charged by a slight temperature change utilizing the difference in temperature coefficient of the redox potential between the cathode and the anode. Secondary batteries are charged by electric power, while tertiary batteries are charged by environmental heat.
- \* 2 Cobalt Prussian blue analogue  
A type of Prussian blue analogue with a chemical composition of  $\text{Na}_x\text{Co}[\text{Fe}(\text{CN})_6]_y$ . The phase transition temperature can be precisely controlled by adjusting the Fe concentration ( $y$ ). Due to its high discharge capacity and high stability, it holds promise also as a material for secondary batteries.
- \* 3 Thermal efficiency  
A physical quantity that represents the efficiency of a heat engine. Defined as [Electric energy generated by the battery] / [Net heat capacity flowing into the battery].
- \* 4 Theoretical efficiency  
The maximum efficiency of a heat engine operating between a high temperature (TH) and a low temperature (TL), expressed as  $1 - \text{TL}/\text{TH}$ . Also known as the Carnot efficiency.
- \* 5 Self-distributed power sources  
A power source that converts natural energy, such as environmental heat, into electric power, with little limitation on installation location. The technology required as the power supply for sensors in Society 5.0. A tertiary battery can be termed one of the self-distributed power sources as it is charged by ubiquitous environmental heat.

Published research paper

Title: Energy harvesting thermocell with use of phase transition  
Authored by: Takayuki Shibata, Hiroki Iwaizumi, Yuya Fukuzumi, and Yutaka Moritomo  
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