

## **Aqueous Vanadium Complex for the Superior Electrolyte of a Thermo-Electrochemical Cell**

Teppei Yamada\*<sup>†‡</sup>, Takashi Kobayashi<sup>§</sup>, Yusuke Wakayama<sup>†</sup>, Fumitoshi Matoba<sup>†§</sup>,  
Koichi Yatsuzuka<sup>||</sup>, Nobuo Kimizuka<sup>§</sup>, Hongyao Zhou<sup>†</sup>,

<sup>†</sup> Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku,  
Tokyo 13-0033, Japan

<sup>‡</sup> CREST, Japan Science and Technology Agency, 102-0076, Japan

<sup>§</sup> Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,  
Motooka 744, Nishi-ku, Fukuoka 819-0035, Japan

<sup>||</sup> Department of Chemistry, Graduate School of Science, Kyushu University Motooka 744, Nishi-ku,  
Fukuoka 819-0035, Japan

## Experimental section:

### Preparation of the sulfuric acid solution of $V^{4+/5+}$ and measurement of the $S_e$

As a buffer for pH and supporting electrolyte, sodium hydrogen sulfate monohydrate (Wako Pure Chemical) was dissolved in distilled water at a concentration of 3 M. To this solution was added 50 mM vanadium(IV) sulfate *n*-hydrate (Wako) and 25 mM vanadium(V) oxide (Wako) as the reductant and the oxidant, respectively. The pH of the solution was adjusted by adding 12.5 M sodium hydroxide solution when needed.

The solution was poured into a house-made H-shaped tube (Fig. S2), and both sides were immersed in an ice-water bath and a water bath to generate a temperature difference ( $\Delta T$ ). Two platinum wires were introduced as electrodes, and the open circuit voltage ( $\Delta V_{oc}$ ) between them was monitored for various  $\Delta T$ .

### Measurement of electrochemical Peltier effect

850  $\mu\text{L}$  of the aqueous  $V^{4+/5+}$  electrolyte adjusted to pH 2.8 was injected into a custom-made electrochemical cell composed of a 1.1 cm-thick PEEK spacer and two platinum plate electrodes. The temperature of one of the electrodes was monitored by a thermistor (104JT-025, SEMITEC, Japan) connected to a source measure unit (SMU, Source Meter 2401, KEITHLEY Instruments, U.S.). Another SMU was used to apply a constant current ( $\pm 1 \text{ mA cm}^{-2}$ ), and the output voltage of the cell was measured. As a comparison, the Peltier effect of an aqueous electrolyte containing 400 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and 400 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]$  was measured too.

### Preparation of $V^{4+/5+}$ in the mixed solution of aqueous sulfate and acetonitrile and measurement of $S_e$

The composition of the electrolyte is shown below. The  $S_e$  was measured as described above.

A mixed solvent of 100 mM sulfuric acid solution and MeCN: MeCN:  $\text{H}_2\text{O}$  = 2:1, 1:1, 1:0 (= v:v)

$\text{VOSO}_4$ : 3.3 mM (MeCN 67%), 5.0 mM, (MeCN 50%), 10 mM (MeCN 0%)

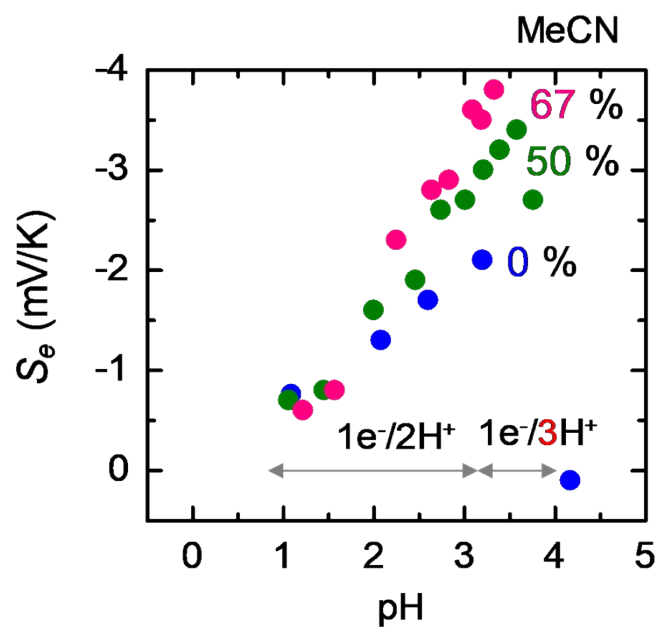
$\text{V}_2\text{O}_5$ : 3.3 mM (MeCN 67%), 5.0 mM, (MeCN 50%), 10 mM (MeCN 0%)

### Miscellaneous measurements

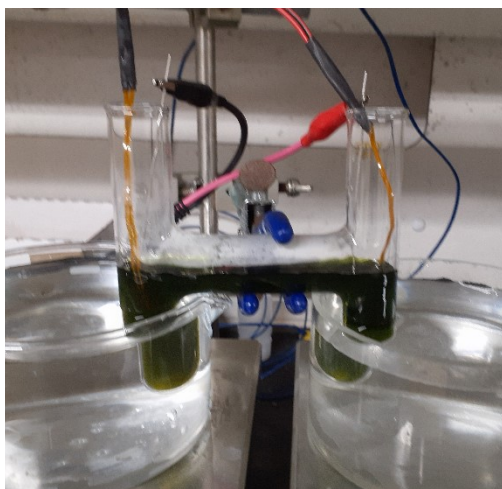
Thermal conductivity was evaluated by a Hot Disk TPS 500 thermal conductivity meter (Kyoto Electronics, Japan) at ambient temperature. The electrical conductivity was measured with a conductivity meter (ES-71, Horiba, Japan).

**Table S1.**  $ZT$  value and related parameters of thermocells

|   | $S_e$ ( $mV K^{-1}$ ) | $\sigma$ ( $mS cm^{-1}$ ) | $\kappa$ ( $W m^{-1} K^{-1}$ ) | $T$ (K) | $ZT$                 |  |
|---|-----------------------|---------------------------|--------------------------------|---------|----------------------|--|
| Vanadium                                | -3.2                  | 97.1                      | 0.62                           | 293     | $4.7 \times 10^{-2}$ |  |
| Ru(biim) <sub>3</sub>                   | -3.7                  | 2.1                       | 0.51                           | 297     | $1.7 \times 10^{-3}$ |  |
| [Fe(CN) <sub>6</sub> ] <sup>3-/4-</sup> | -1.4                  | 190.3                     | 0.55                           | 298     | $2.1 \times 10^{-2}$ |  |



**Figure S1.** Seebeck coefficient of  $V^{4+/5+}$  TEC at various pH conditions in the mixed solution of acetonitrile and aqueous sulfonic acid (Pink: 1:2, Green: 1:1, Blue: 1:0).



**Figure S2.** Photograph of the apparatus of the thermocell measurement.