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High Seebeck Coefficient Electrochemical Thermocells for Efficient Waste Heat Recovery

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Supporting Information

ABSTRACT: An electrochemical thermocell realizes thermal to electric energy conversion when two electrodes operate the same reversible reaction but at different temperatures. Its Seebeck coefficient is determined by the entropy change of the redox reaction. Here we report a thermocell containing acetone and iso-propanol as the redox couple, which can achieve the highest reported Seebeck coefficient of -9.9 mV K⁻¹ when the hot side is above the boiling point of acetone. Vaporization entropy of acetone increases the total entropy change in the conversion of iso-propanol to acetone. In addition, a concentration gradient of acetone caused by



evaporation and condensation increases the cell voltage significantly. Stable performance of the thermocell is enabled by a Pt–Sn catalyst operating in a neutral pH electrolyte solution. The possibility of utilizing a liquid–gas phase change to increase the Seebeck coefficient of thermocells opens a new venue for exploration.

KEYWORDS: thermocell, Seebeck coefficient, electrochemical thermal conversion, temperature coefficient, Pt-Sn catalyst

T he electrochemical potentials of reversible electrode reactions are usually functions of temperature due to entropy changes. This effect can be explored to convert thermal energy into electricity.^{1,2} Thermocells are constructed with identical electrochemical redox pairs on both electrodes which operate at different temperatures. As a result, a voltage is generated in the thermocell.^{3–6} This simple setup and the use of inexpensive materials as compared to solid thermoelectric materials⁷ have stimulated its applications for waste heat recovery,^{3,8,9} as a power source for wearable devices,^{10,11} and as a liquid cooling system.¹²

Seebeck coefficient is a partial derivative of the electrochemical potential with respect to the temperature $(\partial E/\partial T)$.¹³ Much effort has been devoted to maximize this value since a large voltage directly translates to higher thermal efficiency (η) :¹⁴

$$\eta = \frac{\sigma V_{\rm oc}^{\ 2}}{4\kappa\Delta T} \tag{1}$$

 σ and κ are, respectively, the ionic and thermal conductivities of the electrolyte solution. V_{oc} is the open-circuit voltage, and ΔT is the temperature gradient. Consider the following reversible redox reaction: A + $ne^- \rightleftharpoons$ B.

Using the equation for Gibbs free energy and the Nernst equation, the Seebeck coefficient is

$$\frac{\partial E}{\partial T} = -\frac{\Delta S_{\text{redox}} + \Delta S_{\text{vap}}}{nF} + \frac{\partial}{\partial T} \left(\frac{RT}{nF} \ln \left(\frac{c_{A1}}{c_{A2}} \right) \right)$$
(2)

F is the Faraday constant, and *R* is the standard gas constant. *n* is the stoichiometric number of electrons in the redox reaction. ΔS_{redox} and ΔS_{vap} are entropy changes of redox reaction and vaporization, respectively. The first term is negative when oxidation occurs at higher temperatures, and thus the Seebeck coefficient is negative, *vice versa.* c_{A1} and c_{A2} are the respective concentrations of the redox species A in the hot and cold sides of the thermocell, whereas the concentration of the species B is assumed to be constant.¹⁵ ΔS_{redox} of transition metal redox couples was studied by Weaver and co-workers.^{16–19} The solvent effect on ΔS_{redox} and the Seebeck coefficient has also been systematically studied.^{20–22} The Seebeck coefficient can be increased by introducing the concentration difference between c_{A1} and c_{A2} in eq 2, which is previously achieved by exploring host–guest chemistry.^{15,23} However, the Seebeck coefficient is still limited to ca. 2 mV K⁻¹.

The Br₂–Br⁻ thermocell, which was first proposed by Lalancette²⁴ and developed by Endo,²⁵ and Shindo,^{26,27} can exhibit a Seebeck coefficient of 5.68 mV K⁻¹ when the hot side is operated above the boiling point of Br₂.²⁶ The vaporization of Br₂ increases the Seebeck coefficient; however, the extremely corrosive Br₂ vapor limits its application. Previously, a thermally regenerative fuel cell, using hydrogenation of acetone to isopropanol, was studied by Ando and co-workers.^{28–31} A chemical heat pump involving dehydrogenation of iso-propanol and hydrogenation of acetone was studied by Saito and co-

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workers.^{32–35} However, no study on the Seebeck coefficient and thermoelectric power of a thermocell based on this couple has been reported.

Here we demonstrate a thermocell based on the redox couple of acetone and iso-propanol (Figure 1). When the hot



Figure 1. Scheme of the acetone—iso-propanol thermocell. Oxidation of iso-propanol to acetone occurs at the hot side, and the reverse reaction occurs at the cold side. Acetone vaporizes when hot-side temperature is above its boiling point.

side is operated at a temperature above the boiling point of acetone, its vaporization is utilized to create a large concentration difference ($c_{A1}/c_{A2} < 1$). The Seebeck coefficient is raised to -9.9 mV K^{-1} , the highest value reported so far for any redox couple. The thermal efficiency is 1.57% with respect to the Carnot efficiency, which is comparable to the conventional ferri/ferrocyanide redox couple.³⁶ Unlike the Br₂/Br⁻ couple, this redox couple is environmentally benign. Reversible redox reaction of acetone and iso-propanol is observed for the first time in a neutral pH solution. This is essential for the application of thermocells, because self-condensation of acetone occurs in both acidic and basic solutions at elevated temperatures.³⁷

Oxidation of alcohols including iso-propanol on a Snmodified Pt catalyst has been well-studied for the past two decades.^{38–43} However, the reaction is usually conducted in strong acidic solutions. When acetone is heated with strong acid, the self-condensation readily occurs to produce phorone and acetone-derived polymers.³⁷ In addition, the reduction of acetone to iso-propanol on platinum catalysts has not been reported. Here, we electrodeposited a Pt–Sn catalyst on Pt substrate, which forms an aggregation of the nanoparticles with a diameter of 100 nm (Figure 2a, inset). Energy dispersive Xray analysis (EDX) reveals that the atomic ratio of Pt and Sn is 9:2 (Figure 2a).

Cyclic voltammetry of a mixture of acetone and iso-propanol in a neutral pH solution (Figure 2b) shows peaks of reduction of acetone and oxidation of iso-propanol at -0.35 and -0.15 V at 21 °C, respectively. The peak height increases with the square root of the scan rate (Figure S4, Supporting Information), which indicates that the reaction is limited by diffusion of the active species.⁴⁴ The oxidative current of isopropanol increases with temperature, while the reductive peak current of acetone decreases (Figure 2c). Oxidation of one isopropanol molecule produces one acetone and two protons, which increases ΔS_{redox} . Thus, the reaction equilibrium shifts to the acetone side, and oxidation of iso-propanol dominates at



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Figure 2. (a) Energy dispersive X-ray (EDX) analysis of Sn-modified Pt catalyst. The inset shows the scanning electron microscopy (SEM) image, and EDX was performed at the selected area. (b) Hydrogenation/dehydrogenation of acetone and iso-propanol on the Pt–Sn electrode at 21 °C with various scan rates. The first three cycles of cyclic voltammetry of an aqueous solution of acetone and iso-propanol (10 vol % each) with 1 M Li₂SO₄ as the supporting electrolyte are shown. Baseline = aqueous solution of 1 M Li₂SO₄. (c) Cyclic voltammetry when the temperature was raised from 21, to 48, and to 69 °C. Scan rate = 50 mV s⁻¹.

higher temperatures. These results indicate that a thermocell with iso-propanol oxidation on the hot side and acetone reduction on the cold side is expected to generate power.

Open-circuit voltage (V_{oc}) increases linearly with increasing temperature differences between the hot and cold sides (Figure 3a). The Seebeck coefficient is evaluated as a slope of the leastsquares fitting to the V_{oc} . The Seebeck coefficient is -3.4 mV K^{-1} , between $\Delta T = 0$ and 40 K; however, the value increases to $-9.9 \text{ mV} \text{ K}^{-1}$ as ΔT exceeds 40 K. We found out that the heating of the gas bridge which connects the hot-side and coldside cells promotes the mass transfer of acetone vapor and is essential for the increase of the Seebeck coefficient (Figure S5, Supporting Information). Because acetone evaporates from the hot side, $c_{A1}/c_{A2} < 1$ in eq 2, and the Seebeck coefficient shift to negative values. The concentrations of iso-propanol in the hot side and cold side are approximated to be equal, because the vapor pressure of iso-propanol is much smaller than that of acetone (Figure S7a, Supporting Information).

 ΔS_{redox} is evaluated as 656 J K⁻¹ mol⁻¹ from the Seebeck coefficient (-3.4 mV K⁻¹) at $\Delta T < 40$ K, where vaporization of acetone is negligible. Duan and co-workers⁴⁵ evaluated ΔS_{vap} of acetone in water as 230 J K⁻¹ mol⁻¹. According to eq 2, ΔS_{vap} contributes to the increase of Seebeck coefficient by -1.2 mV K⁻¹, as indicated in Figure 3b. We evaluated the partial pressure and the concentration of acetone in the hot-side cell from Henry's law⁴⁶ (Figure S7b,c, Supporting Information). The partial pressure of acetone vapor increases significantly at $\Delta T > 40$ K, and acetone vapor starts diffusing from the hot-side cell to the cold-side cell. The concentration gradient has a greater contribution to the increase of the Seebeck coefficient compared to the vaporization entropy (Figure 3b).

The Seebeck coefficient and working temperature of the thermocell are evaluated in this study, and the results reported in the recent literature are summarized in Figure 3c. As



Figure 3. (a) Open-circuit voltage of the hot-side electrode vs the cold-side electrode in an acetone–iso-propanol thermocell. Experimental data obtained from the two thermocells is plotted. The cold-side temperature is maintained at 20–23 °C. Seebeck coefficient is evaluated from the least-squares fitting. (b) Simulation results of the additional voltage due to the vaporization entropy (ΔS_{vap} term) and the concentration gradient (Nernst term) calculated from eq 2. The sum of the two terms agrees with the experimental results in part a. (c) Comparison between the Seebeck coefficient (absolute value) and the working temperature of acetone–iso-propanol thermocell (red), and those of other redox systems (blue): Fe(CN)₆^{3-/4-} = ferri/ferrocyanide;³⁶ Co(bpy)₃^{2+/3+} = cobalt trisbipyridyl;²⁰ I₃⁻/I⁻ + α -CD (α -cyclodextrin as a host molecule);¹⁵ Br₂/Br^{-2.6} Vaporization of acetone realizes the highest Seebeck coefficient.

mentioned above, Seebeck coefficients of most of redox couples are limited to around 2 mV K⁻¹. Although the Br₂/Br⁻ redox couple exhibits a high Seebeck coefficient, the working temperature is confined in a narrow range, because the $V_{\rm oc}$ rapidly decays to zero below 50 °C.²⁶

An acetone–iso-propanol thermocell exhibits a high Seebeck coefficient (-3.4 mV K^{-1}) even below the boiling point of acetone (20-60 °C), which effectively increases the range of working temperature. Above 60 °C, the phase change of acetone from the liquid to the gas state increases the Seebeck coefficient by a factor of 3, reaching the highest value ever reported. The working temperature of the organic thermocell can be tailored by selecting the redox species with different boiling points. For example, quinone-related compound, which has been used in organic redox flow batteries,^{47,48} possibly increases the working temperature above 100 °C.

Linear-sweep voltammetry (LSV) shows that output current increases with increasing temperature differences (Figure 4a). The slopes of current—voltage lines are the same, indicating the resistance of the cell is unchanged with temperature. Cyclic voltammetry (CV) at $\Delta T = 50$ K (Figure 4b) shows a reversible current—voltage profile. It is noteworthy that, in LSV measurement, capacitive current (non-Faradaic current) can increase the total current, while CV measurement uses a staircase-voltage step (current is measured after voltage change) to minimize the influence of capacitive current. The current—



Figure 4. I-V plot and stability of acetone–iso-propanol thermocell. (a) Linear-sweep voltammetry of the thermocell at various temperature differences applied. Scan rate = 10 mV s⁻¹. Each line is scanned from the open-circuit voltage. (b) Cyclic voltammetry of the thermocell at the temperature difference of 50 K. Each cycle is scanned from the open-circuit voltage to 10 mV. (c) Chronoamperometry of the thermocell discharged at 0, 50, and 100 mV for 1 h, respectively, and (d) the thermocell discharged at 70 mV for 60 h. Current values between each dot were averaged for clarity, and error bars indicate the standard deviation. Active area of the Pt–Sn electrode was 0.5 cm² (a–d).

voltage profiles at a scan rate of 5 and 50 mV s⁻¹ overlap, indicating that the current is limited by Ohmic resistance of the cell, which is calculated as 11.5 k Ω . This high Ohmic resistance may be due to the long distance between the hot-side and coldside electrodes (18 cm), which is designed to reduce the heat flux from the hot side and realizes the large ΔT in our setup. At a slower scan rate (1 mV s⁻¹), reaction kinetics of acetone/isopropanol starts to limit the output current, and the current– voltage profile deviates from linearity. The output current can be improved by optimizing the cell dimension and decreasing the distance between the electrodes.⁴⁹

The output current measured by chronoamperometry at discharge voltages of 0, 50, 100 mV (Figure 4c) qualitatively agrees with the current–voltage profile (Figure 4b). The output current at discharge voltage of 70 mV lasts for 60 h without degradation, indicating that the Pt–Sn electrode is free from poisoning of acetone/iso-propanol, and the concentration gradient of acetone is maintained. Neutral pH solution is the key for the long-term stable operation, whereas a precipitation of self-polymerized acetone was observed in the sulfuric acid solution (Figure S9, Supporting Information).

The ionic conductivity of the acetone—iso-propanol electrolyte was evaluated as 40 mS cm⁻¹ at 47 °C (Figure S10, Supporting Information). Thermal efficiency of the thermocell discharged at 70 °C versus 23 °C is calculated from eq 1 (see Supporting Information for the full derivations). The absolute efficiency is $\eta = 0.215\%$, which is 1.57% of the Carnot efficiency. This value is comparable to the previously reported efficiency of the Fe(CN)₆^{3-/4-} redox couple.³⁶ In summary, the Seebeck coefficient of the acetone—iso-

In summary, the Seebeck coefficient of the acetone–isopropanol redox couple is reported, which increases from -3.4

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mV K^{-1} to an unprecedented value of -9.9 mV K^{-1} above the boiling point of acetone. We circumvented the problematic poisoning of the catalyst, and self-condensation reaction of acetone, by using a Sn-modified Pt catalyst, and a neutral pH solution, respectively. In addition, the neutral pH solution is free from corrosion and enables the use of metal containers, which will facilitate the cell design.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b00247.

Experimental details, the setup of the thermocell, and theoretical discussions on the vaporization rate of acetone and the thermal efficiency (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Lee, S. W.; Yang, Y.; Lee, H.-W.; Ghasemi, H.; Kraemer, D.; Chen, G.; Cui, Y. An Electrochemical System for Efficiently Harvesting Low-Grade Heat Energy. *Nat. Commun.* **2014**, 5 (May), 3942.

(2) Yang, Y.; Lee, S. W.; Ghasemi, H.; Loomis, J.; Li, X.; Kraemer, D.; Zheng, G.; Cui, Y.; Chen, G. Charging-Free Electrochemical System for Harvesting Low-Grade Thermal Energy. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111* (48), 17011–17016.

(3) Dupont, M. F.; MacFarlane, D. R.; Pringle, J. M. Thermo-Electrochemical Cells for Waste Heat Harvesting – Progress and Perspectives. *Chem. Commun.* **2017**, *53*, 6288–6302.

(4) Quickenden, T. I.; Mua, Y. A Review of Power Generation in Aqueous Thermogalvanic Cells. J. Electrochem. Soc. **1995**, 142 (11), 3985–3994.

(5) Chum, H. L.; Osteryoung, R. A. Review of Thermally Regenerative Electrochemical Systems. *Rep. SERI/TR- 332416;* US DOE OSTI, 1980; Vol. 1. DOI: 10.2172/5030338

(6) Ikeshoji, T.; de Nahui, F. N. B. New Electrochemical System of High Thermoelectric Power. J. Electroanal. Chem. Interfacial Electrochem. 1991, 305 (1), 147–151.

(7) Twaha, S.; Zhu, J.; Yan, Y.; Li, B. A Comprehensive Review of Thermoelectric Technology: Materials, Applications, Modelling and Performance Improvement. *Renewable Sustainable Energy Rev.* 2016, 65, 698–726.

(8) Im, H.; Kim, T.; Song, H.; Choi, J.; Park, J. S.; Ovalle-Robles, R.; Yang, H. D.; Kihm, K. D.; Baughman, R. H.; Lee, H. H.; Kang, T. J.; Kim, Y. H. High-Efficiency Electrochemical Thermal Energy Harvester Using Carbon Nanotube Aerogel Sheet Electrodes. *Nat. Commun.* **2016**, *7*, 10600. (9) Zhang, L.; Kim, T.; Li, N.; Kang, T. J.; Chen, J.; Pringle, J. M.; Zhang, M.; Kazim, A. H.; Fang, S.; Haines, C.; Al-Masri, D.; Cola, B. A.; Razal, J. M.; Di, J.; Beirne, S.; MacFarlane, D. R.; Gonzalez-Martin, A.; Mathew, S.; Kim, Y. H.; Wallace, G.; Baughman, R. H. High Power Density Electrochemical Thermocells for Inexpensively Harvesting Low-Grade Thermal Energy. *Adv. Mater.* **2017**, *29* (12), 1605652.

(10) Yang, P.; Liu, K.; Chen, Q.; Mo, X.; Zhou, Y.; Li, S.; Feng, G.; Zhou, J. Wearable Thermocells Based on Gel Electrolytes for the Utilization of Body Heat. *Angew. Chem., Int. Ed.* **2016**, *55* (39), 12050–12053.

(11) Chang, W. B.; Evans, C. M.; Popere, B. C.; Russ, B. M.; Liu, J.; Newman, J.; Segalman, R. A. Harvesting Waste Heat in Unipolar Ion Conducting Polymers. *ACS Macro Lett.* **2016**, *5*, 94–98.

(12) Kazim, A. H.; Booeshaghi, A. S.; Stephens, S. T.; Cola, B. A. Thermo-Electrochemical Generator: Energy Harvesting & Thermoregulation for Liquid Cooling Applications. *Sustain. Energy Fuels* **2017**, *1*, 1381.

(13) Salazar, P. F.; Kumar, S.; Cola, B. A. Design and Optimization of Thermo-Electrochemical Cells. *J. Appl. Electrochem.* **2014**, *44* (2), 325–336.

(14) Ikeshoji, T. Thermoelectric Conversion by Thin-Layer Thermogalvanic Cells with Soluble Redox Couples. *Bull. Chem. Soc. Jpn.* **1987**, *60* (4), 1505–1514.

(15) Zhou, H.; Yamada, T.; Kimizuka, N. Supramolecular Thermo-Electrochemical Cells: Enhanced Thermoelectric Performance by Host–Guest Complexation and Salt-Induced Crystallization. *J. Am. Chem. Soc.* **2016**, *138*, 10502–10507.

(16) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. A Survey of Ligand Effects upon the Reaction Entropies of Some Transition Metal Redox Couples. *J. Am. Chem. Soc.* **1979**, *101* (5), 1131–1137.

(17) Sahami, S.; Weaver, M. J. Entropic and Enthalpic Contributions To the Solvent Dependence of the Thermodynamics of Transition-Metal Redox Couples Part I. Couples Containing Aromatic Ligands. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *122*, 155–170.

(18) Sahami, S.; Weaver, M. J. Entropic and Enthalpic Contributions To the Solvent Dependence of the Thermodynamics of Transition-Metal Redox Couples Part II. Couples Containing Amine and Ethylenediamine Ligands. J. Electroanal. Chem. Interfacial Electrochem. **1981**, 122, 171–181.

(19) Hupp, J.; Weaver, M. Solvent, Ligand, and Ionic Charge Effects on Reaction Entropies for Simple Transition-Metal Redox Couples. *Inorg. Chem.* **1984**, *23*, 3639–3644.

(20) Abraham, T. J.; MacFarlane, D. R.; Pringle, J. M. High Seebeck Coefficient Redox Ionic Liquid Electrolytes for Thermal Energy Harvesting. *Energy Environ. Sci.* **2013**, *6*, 2639–2645.

(21) Lazar, M. A.; Al-Masri, D.; MacFarlane, D. R.; Pringle, J. M. Enhanced Thermal Energy Harvesting Performance of a Cobalt Redox Couple in Ionic Liquid-Solvent Mixtures. *Phys. Chem. Chem. Phys.* **2016**, *18*, 1404–1410.

(22) Kim, T.; Lee, J. S.; Lee, G.; Yoon, H.; Yoon, J.; Kang, T. J.; Kim, Y. H. High Thermopower of Ferri/ferrocyanide Redox Couple in Organic-Water Solutions. *Nano Energy* **2017**, *31*, 160–167.

(23) Zhou, H.; Yamada, T.; Kimizuka, N. Thermo-Electrochemical Cells Empowered by Selective Inclusion of Redox-Active Ions by Polysaccharides. *Sustain. Energy Fuels* **2018**, *2*, 472–478.

(24) Lalancette, J.-M.; Roussel, R. Metals Intercalated in Graphite. V. A Concentration Cell with Intercalated Bromine. *Can. J. Chem.* **1976**, *54* (22), 3541–3544.

(25) Endo, M.; Yamagishi, Y.; Inagaki, M. Thermocell with Graphite Fiber-Bromine Intercalation Compounds. *Synth. Met.* **1983**, 7 (3–4), 203–209.

(26) Shindo, K.; Arakawa, M.; Hirai, T. Effect of Non-Graphitized Carbon Electrodes on the Electrochemical Characteristics of a Thermocell with a Br2/Br– Redox Couple. *J. Power Sources* **1998**, 70 (2), 228–234.

(27) Shindo, K.; Arakawa, M.; Hirai, T. Influence of Electrode Materials on Open-Circuit Voltage Profiles with a Temperature

ACS Applied Energy Materials

Difference for a Thermocell Using a Br2/Br–Redox Reaction. J. Power Sources 2002, 110 (1), 46–51.

(28) Ando, Y.; Tanaka, T.; Doi, T.; Takashima, T. A Study on a Thermally Regenerative Fuel Cell Utilizing Low-Temperature Thermal Energy. *Energy Convers. Manage.* **2001**, *42* (15–17), 1807–1816.

(29) Ando, Y.; Aoyama, Y.; Sasaki, T.; Saito, Y.; Hatori, H.; Tanaka, T. Effect of Catalytic and Electrochemical Acetone Hydrogenation on the I-V Characteristics of an Acetone/hydrogen-Based Thermally Regenerative Fuel Cell. *Bull. Chem. Soc. Jpn.* **2004**, 77 (10), 1855–1859.

(30) Ando, Y.; Tanaka, T.; Amano, M. Influence of the Internal Structure and Temperature in the Reaction Layer on the Electric Output in a Solar Thermal Cell. *Energy Convers. Manage.* **2003**, *44* (17), 2811–2819.

(31) Chaurasia, P. B. L.; Ando, Y.; Tanaka, T. Investigation on Proton Exchange Membrane Fuel Cell for Solar Power Generation. *Int. J. Sustain. Energy* **2007**, *26* (2), 107–119.

(32) Saito, Y.; Kameyama, H.; Yoshida, K. Catalyst-assisted Chemical Heat Pump with Reaction Couple of Acetone hydrogenation/2–propanol Dehydrogenation for Upgrading Low-level Thermal Energy: Proposal and Evaluation. *Int. J. Energy Res.* **1987**, *11* (4), 549–558.

(33) Noda, M.; Shinoda, S.; Saito, Y. Liquid-Phase Dehydrogenation of 2-Propanol by Suspended Nickel Fine-Particle Catalyst. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 961–965.

(34) Saito, Y.; Yamashita, M.; Ito, E.; Meng, N. Hydrogen Production from 2-Propanol as a Key Reaction for a Chemical Heat Pump with Reaction Couple of 2-Propanol Dehydrogenation/acetone Hydrogenation. *Int. J. Hydrogen Energy* **1994**, *19* (3), 223–226.

(35) Meng, N.; Shinoda, S.; Saito, Y. Improvements on Thermal Efficiency of Chemical Heat Pump Involving the Reaction Couple of 2-Propanol Dehydrogenation and Acetone Hydrogenation. *Int. J. Hydrogen Energy* **1997**, *22* (4), 361–367.

(36) Hu, R.; Cola, B. A.; Haram, N.; Barisci, J. N.; Lee, S.; Stoughton, S.; Wallace, G.; Too, C.; Thomas, M.; Gestos, A.; Dela Cruz, M. E.; Ferraris, J. P.; Zakhidov, A. a.; Baughman, R. H. Harvesting Waste Thermal Energy Using a Carbon-Nanotube-Based Thermo-Electrochemical Cell. *Nano Lett.* **2010**, *10* (3), 838–846.

(37) Cataldo, F. Synthesis of Ketonic Resins from Self-Polymerization of Acetone, 1. Action of Protic and Lewis Acids on Acetone. *Angew. Makromol. Chem.* **1996**, 236 (1), 1–19.

(38) Gonzalez, M. J.; Hable, C. T.; Wrighton, M. S. Electrocatalytic Oxidation of Small Carbohydrate Fuels at Pt-Sn Modified Electrodes. *J. Phys. Chem. B* **1998**, *102*, 9881–9890.

(39) Zhou, W. J.; Song, S. Q.; Li, W. Z.; Zhou, Z. H.; Sun, G. Q.; Xin, Q.; Douvartzides, S.; Tsiakaras, P. Direct Ethanol Fuel Cells Based on PtSn Anodes: The Effect of Sn Content on the Fuel Cell Performance. *J. Power Sources* **2005**, *140* (1), 50–58.

(40) Antolini, E. Catalysts for Direct Ethanol Fuel Cells. J. Power Sources 2007, 170 (1), 1–12.

(41) Zhu, M.; Sun, G.; Xin, Q. Effect of Alloying Degree in PtSn Catalyst on the Catalytic Behavior for Ethanol Electro-Oxidation. *Electrochim. Acta* **2009**, *54* (5), 1511–1518.

(42) Puthiyapura, V. K.; Brett, D. J. L.; Russell, A. E.; Lin, W. F.; Hardacre, C. Biobutanol as Fuel for Direct Alcohol Fuel Cells-Investigation of Sn-Modified Pt Catalyst for Butanol Electro-Oxidation. *ACS Appl. Mater. Interfaces* **2016**, 8 (20), 12859–12870.

(43) Wei, Z. D.; Li, L. L.; Luo, Y. H.; Yan, C.; Sun, C. X.; Yin, G. Z.; Shen, P. K. Electrooxidation of Methanol on Upd-Ru and Upd-Sn Modified Pt Electrodes. *J. Phys. Chem. B* **2006**, *110* (51), 26055–26061.

(44) Huang, T.; Mao, S.; Zhou, G.; Zhang, Z.; Wen, Z.; Huang, X.; Ci, S.; Chen, J. A High-Performance Catalyst Support for Methanol Oxidation with Graphene and Vanadium Carbonitride. *Nanoscale* **2015**, 7 (4), 1301–1307.

(45) Duan, S. X.; Jayne, J. T.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. Uptake of Gas-Phase Acetone by Water Surfaces. J. Phys. Chem. **1993**, 97 (10), 2284–2288. (46) Sander, R. Compilation of Henry's Law Constants (Version 4.0) for Water as Solvent. *Atmos. Chem. Phys.* **2015**, *15* (8), 4399–4981.

(47) Huskinson, B.; Marshak, M. P.; Suh, C.; Er, S.; Gerhardt, M. R.; Galvin, C. J.; Chen, X.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J. A Metal-Free Organic-Inorganic Aqueous Flow Battery. *Nature* **2014**, 505 (7482), 195–198.

(48) Lin, K.; Chen, Q.; Gerhardt, M. R.; Tong, L.; Kim, S. B.; Eisenach, L.; Valle, A. W.; Hardee, D.; Gordon, R. G.; Aziz, M. J.; Marshak, M. P. Alkaline Quinone Flow Battery. *Science (Washington, DC, U. S.)* **2015**, 349 (6255), 1529–1532.

(49) Mua, Y.; Quickenden, T. I. Power Conversion Efficiency, Electrode Separation, and Overpotential in the Ferricyanide/ Ferrocyanide Thermogalvanic Cell. *J. Electrochem. Soc.* **1996**, *143* (8), 2558–2564.