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ABSTRACT

Practical conversion of waste heat into electricity via thermoelectrochemical cells requires high Seebeck coefficient (α) to increase cycle efficiency. The complexation of Cu^{2+} species with dissolved multidentate ligands, such as ethylenediaminetetraacetic acid, and the control of dimerization equilibria with bridging ligands, such as 1,6-diaminohexane or 1,2-diaminoethane, dramatically improve, by up to ~185%, the magnitude of the α of Cu/Cu^{2+} thermoelectrochemical cells. This results in the highest α for any Cu/Cu^{2+} redox system yet reported. The coefficient α is directly proportional to the change in entropy (ΔS). It was experimentally measured and correlated with ΔS obtained from quantum-chemical methods. This offers a deeper insight about a molecule-based interpretation of the macroscopic response. The agreement between the theoretically estimated and experimentally observed α is remarkable. Hence, we believe that this synergistic approach allows us to systematically scan different systems to obtain efficient thermoelectrochemical cells with enhanced Seebeck coefficient.

Waste heat energy conversion remains an important subject for research, given the enhanced emphasis on energy efficiency and carbon emissions reduction. Solid-state thermoelectric devices have been widely investigated, but their practical application remains challenging because of cost and the inability to fabricate them in geometries that are easily compatible with heat sources.[1] An emerging and promising alternative to thermoelectric devices is thermoelectrochemical cells, also known as thermogalvanic cells or simply as thermocells.[2] The thermal temperature coefficient of the electrode potential (α) of a thermoelectrochemical cell is directly proportional to the change in entropy (ΔS) of the redox reaction in the cell through the relation $\alpha = \partial E/\partial T = \Delta S/nF$, where E is the cell potential, T the temperature, n the number of electrons involved in the redox reaction, and F the Faraday constant. Although the physical origins of thermal effects for thermoelectrics and thermoelectrochemical cells are different, α is often referred to as the Seebeck coefficient (of a thermoelectrochemical cell).[3]

Ideally, the redox couple for a thermoelectrochemical cell should have high intrinsic Seebeck coefficient.[1–4] However, identifying such an ideal system is not an easy task. There are many available options, including commercial and custom synthesized compounds. As described in our recent review article,[5] between 1995 and 2013 four studies reported results using molten salt and ionic liquids, two reported results for non-aqueous (organic) redox couple electrolytes, and six described continuing work with aqueous redox couples. A subsequent review, minireview, and perspectives article[2,6–11] that compiled and discussed creditable progress made to improve α since 2013 are also available. Two notable examples are the use of α-cyclodextrin supramolecule to improve the α of the I_3^-/I^- redox system from 0.86 to 1.97 mV K^{-1},[12] and the addition of guanidium cations into the benchmark $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ aqueous redox system, which induces thermosensitive crystallization and dissolution processes, that amplifies the α from 1.4 to 3.73 mV K^{-1}.[1] However, it still remains challenging to develop new and rational methodologies that can substantially enhance the α value.[6,12,13]

In the current study, we show that coupling the Cu/Cu^{2+} redox process to solution-phase complexation increases the entropy change

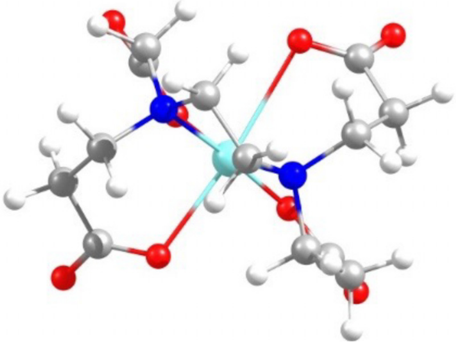

FIG. 1. Cu^{2+}–EDTA complex.

(ΔS) for the electron transfer process. The concept is to complex the Cu^{2+} species with a multidentate ligand, such as ethylenediaminetetraacetic acid (EDTA). As indicated by Weaver *et al.*,[14–17] this allows taking advantage of entropy changes inherent to the complexation process as part of the entropy change for the overall redox process. This approach opens another previously unexplored variable space for the control of entropies of redox reactions in thermoelectrochemical cells.

We chose to focus on the Cu/Cu^{2+} cell because we already have considerable experience with the Cu/Cu^{2+} system,[5,18,19] which has a relatively simple electrochemical behavior. We have used EDTA as the complexing ligand because of the availability of previous reports of entropies associated with various forms of Cu^{2+} EDTA complexes.[20,21] As shown in Fig. 1, the Cu^{2+} ion can be chelated with ligands, such as ethylenediaminetetraacetic acid (EDTA)[20] to produce a very stable complex. This changes the reduction potential for the Cu(II)/Cu redox couple as a consequence of the high formation constant for the complex, $6.3 \times 10^{18}\ M^{-1}$.[22]

The same apparatus from the previous study[5] was used for the experiments (Fig. 2). The electrolyte was contained in two 10-ml glass beakers, with a stopper holding an electrode and a thermocouple in each beaker. A 14-cm-long tube with inner diameter of 1/8-in. (Tygon R-3603, Cole-Parmer, Vernon Hills, IL) filled with the same electrolyte connected the two beakers as a salt bridge. A Keithley 6517B Electrometer/High Resistance Meter was used to measure the cell potentials. A thermoelectric cooler (TE Technology, Inc. CP-031) was attached at the bottom of the hot beaker with Arctic Silver thermal paste (Arctic Silver, Inc., Visalia, CA) to enhance heat conductance. The thermoelectric cooler was controlled by a programmable Newport 3040 temperature controller. The cold side was maintained at room temperature by natural cooling. OMEGA hermetically sealed type-T thermocouples were connected to a Campbell Scientific CR23X Micrologger to monitor and record temperature differences. This temperature measurement system was calibrated, and its mean relative error was estimated to be ±1.0%, with a maximum uncertainty of ±1.3%.

Copper sulfate ($CuSO_4$) solution was prepared by dissolving 99% purity $CuSO_4{\cdot}5H_2O$ salt (PTI Process Chemicals, Ringwood, IL) into de-ionized water. The metal complex solution was prepared by dissolving ethylenediaminetetraacetic acid disodium salt dihydrate (Sigma-Aldrich, 99%–101%), and 1,6-diaminohexane (Sigma-Aldrich, 98%) or 1,2-diaminoethane (Sigma-Aldrich, $\geq$99%) into the $CuSO_4$ aqueous solution, and stirring the solution slowly. After the stirring process, K_2SO_4 (Strem Chemicals Inc., $\geq$99%) was added into the solution as a background electrolyte. 0.1 H_2SO_4 (Amresco, >95% purity) or 0.1 M NaOH (LabChem Inc., USA) was used to adjust pH of the solution (see details in the supplementary material). pH and ionic conductivity (Fig. S1 in the supplementary material) of the solution was measured using a Hach EC10 pH Meter and a Hach CO150 Conductivity Meter, respectively. The 30-cm long Cu electrodes were prepared by winding 22 American Wire Gauge bare copper wires (99.9%, Arcor Electronics, Northbrook, IL). The Cu electrodes were rinsed with methanol and de-ionized water at the onset of each experiment and were used immediately after air drying.

After the electrolyte was mixed into the cell, the cell was left idle (usually for 30 min) to allow the cell's open-circuit potential (E_{oc}) to reach steady state. Once the E_{oc} reading reached steady state, the hot electrode was heated up and the temperature difference (ΔT) between the hot and the cold electrode was maintained at 10 °C. After the ΔT and E_{oc} readings became steady, i.e., when the readings varied

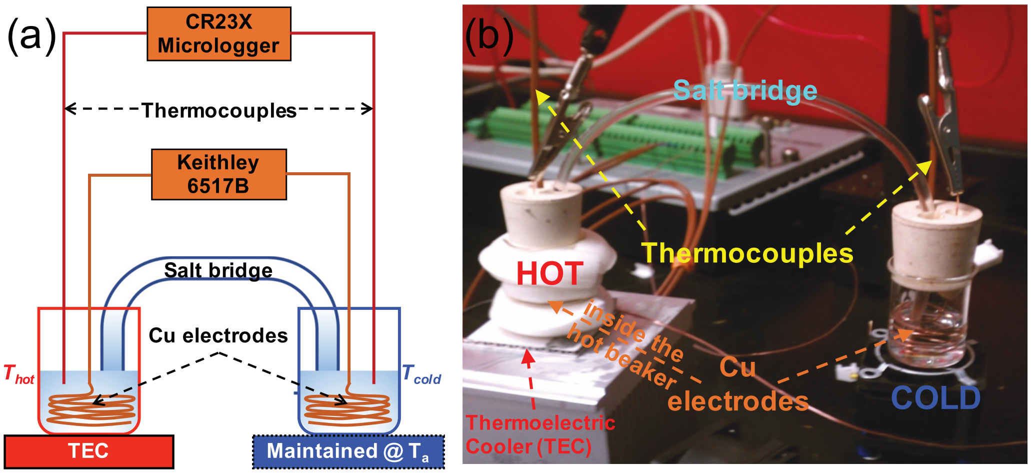

FIG. 2. (a) Schematic diagram of experimental configuration. (b) Photograph of the experimental configuration.

between ±0.3 °C and ±2.5 mV over the average values, respectively, the hot electrode was heated up to the next ΔT of 20 °C. This usually required another 55–65 min. The same procedure was repeated for the following ΔT's of 30 and 40 °C. In addition, for a reversibility check, the ΔT was consecutively decreased to 30, 20, 10, and back to 0 °C by following the same procedure, but with less time (~40 min) between temperature changes. The Seebeck coefficient was determined by averaging the E_{oc} readings at each ΔT, taken during an appropriate time interval that corresponds to the steady criteria described above.

We use a low concentration of $CuSO_4$ (i.e., 1 mM) to avoid precipitation issues with any of the reaction components. For a first approximation, we calculate the Seebeck coefficient of 1 mM $CuSO_4$ aqueous solution $\alpha = \partial E^0/\partial T + (R/nF)\ln(C_{\mathrm{Cu}^{2+}}) = 0.581\ \mathrm{mV\,K^{-1}}$, from deBethune *et al.*,[23] where $\partial E^0/\partial T = 0.879\ \mathrm{mV\,K^{-1}}$ is the Seebeck coefficient of a standard Cu/Cu^{2+} cell at 25 °C, $n = 2$ the number of electrons involved in the redox reaction, $C_{\mathrm{Cu}^{2+}} = 0.001$ the molar concentration of the $CuSO_4$ aqueous solution (i.e., 1 mM), and the remaining terms have their usual meanings.

A preliminary experiment was subsequently done to validate the calculated value of $\alpha = 0.581\ \mathrm{mV\,K^{-1}}$. As noted by deBethune *et al.*,[23] the calculation agrees very well within $\pm 0.05\ \mathrm{mV\,K^{-1}}$ with the experimental value depicted in Fig. 3(a) ($\alpha = 0.569\ \mathrm{mV\,K^{-1}}$). It also follows the trend of α for various $CuSO_4$ concentrations (Fig. S2) that we reported in one of our separate publications[5] very well. We, therefore, use the experimental value of $\alpha = 0.569\ \mathrm{mV\,K^{-1}}$ as a benchmark for the following discussion.

As mentioned earlier, we used EDTA to explore the role of the complexation entropy change in the generation of thermoelectric power. Non-zero background voltage was observed at $\Delta T = 0$ °C; similar observations have been reported in the literature.[24,25] In addition, the α for the EDTA and the following experiments was determined by averaging only the E_{oc} readings at each ΔT during the cooldown period, because during the warm-up period most of the E_{oc} readings,

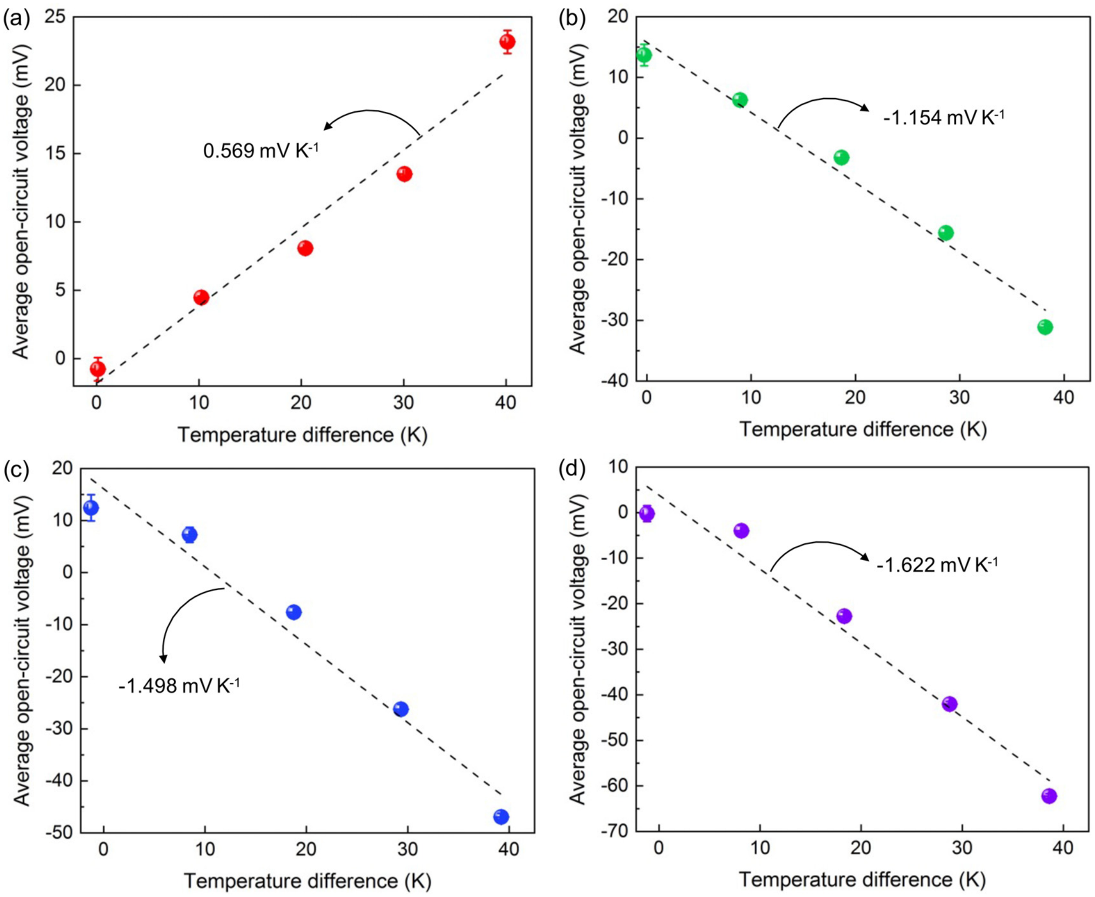

FIG. 3. (a) Baseline Seebeck coefficient of 1 mM $CuSO_4$ aqueous electrolyte in a thermoelectrochemical cell with Cu electrodes. The solution contained 0.1 M potassium sulfate and was adjusted to pH 5, from the natural pH of ~5.7, using 0.1 M sulfuric acid. (b) Seebeck coefficient of 10 mM EDTA + 1 mM $CuSO_4$. The solution contained 0.1 M potassium sulfate and was adjusted to pH 6, from the natural pH of ~3.6, using 0.1 M sodium hydroxide. (c) Seebeck coefficient of 0.5 mM $(NH_2)_2(CH_2)_6$ + 10 mM EDTA + 1 mM $CuSO_4$. The solution contained 0.1 M potassium sulfate and was adjusted to pH 6, from the natural pH of ~4, using 0.1 M sodium hydroxide. (d) Seebeck coefficient of 0.5 mM $(NH_2)_2(CH_2)_2$ + 10 mM EDTA + 1 mM $CuSO_4$. The solution contained 0.1 M potassium sulfate and was adjusted to pH 6, from the natural pH of ~4, using 0.1 M sodium hydroxide. Error bars represent standard deviations from repeated measurements. Some error bars are not visible because they are smaller than the corresponding markers.

especially at $\Delta T = 10\,^{\circ}\mathrm{C}$, were not following the standard linear $\partial E/\partial T$ behavior. Figure 3(b), therefore, shows results, demonstrating that the averaged experimental run of Cu-EDTA aqueous electrolyte gives a Seebeck coefficient of $|\alpha| = 1.154\,\mathrm{mV\ K^{-1}}$. This doubles the standard 1 mM $CuSO_4$ result of $0.569\,\mathrm{mV\ K^{-1}}$ and is the highest Seebeck coefficient for any Cu/Cu^{2+} redox system yet reported.

We further explored the unusually large entropic contributions from dimerization. In these dimers, two Cu(II)EDTA centers are bridged by nitrogen coordination from a α,ω-diamine, such as 1,6-diaminohexane. This makes available the especially large entropy changes for such dimerization reactions.[20,21] These papers suggested that, for example, adding half a mole fraction of 1,6-diaminohexane, i.e., $H_2N(CH_2)_6NH_2$, into the Cu-EDTA experiments would result in a dimeric species of $EDTACu–H_2N(CH_2)_6NH_2–CuEDTA$. In such a case, the formation of the dimeric species results in a large negative entropy change (ΔS), $-696.2\,\mathrm{J\,mol^{-1}\,K^{-1}}$, that can be additive to the overall redox reaction so long as the dimer is the final product of oxidation. Hupp and Weaver indicated that the negative entropy changes can be attributed to the charge numbers of the oxidized forms being larger than the reduced forms and vice versa.[16] Similarly, 1,2-diaminoethane produces a change in the entropy of $-626.1\,\mathrm{J\ mol^{-1}\ K^{-1}}$, a slightly smaller, but still negative, entropy change.

To examine this, a minimum of four independent experiments were evaluated for each of the diamine "additives." The results are shown in Figs. 3(c) and 3(d), respectively. Figure 3(c) shows that simply adding a half mole fraction of 1,6-diaminohexane into a Cu-EDTA aqueous electrolyte further increases the Seebeck coefficient of traditional 1 mM $CuSO_4$ aqueous electrolyte up to $|\alpha| = 1.498\,\mathrm{mV\ K^{-1}}$, which is ∼160% larger than the value for the standard Cu/Cu^{2+} redox couple of 0.569 mV $\mathrm{K^{-1}}$. It is higher than the benchmark value of $|\alpha| = 1.4\,\mathrm{mV\ K^{-1}}$, which is the Seebeck coefficient of ferro/ferricyanide $[Fe(CN)_6{}^{4-}/Fe(CN)_6{}^{3-}]$ aqueous electrolyte.[26–28] Moreover, adding the same half mole fraction of 1,2-diaminoethane, i.e., $H_2N(CH_2)_2NH_2$, into a Cu-EDTA aqueous electrolyte amplifies the Seebeck coefficient to an even higher value of $|\alpha| = 1.622\,\mathrm{mV\ \ K^{-1}}$. This value almost triples that of the standard Cu/Cu^{2+} redox couple. These Seebeck coefficient values together with their corresponding change in entropies and the estimated Seebeck coefficients $\alpha[\mathrm{mV\,K^{-1}}] = \Delta S\left[\mathrm{J\,mol^{-1}\,K^{-1}}\right] \times 1000/nF$, where the number of electrons n equals 4 for the $(CuEDTA)_2(NH_2)_2(CH_2)_2{}^{4-}$ and $(CuEDTA)_2(NH_2)_2(CH_2)_6{}^{4-}$ complexes, and the Faraday constant $F = 96\,485\,\mathrm{C\,mol^{-1}}$, are tabulated in Table I for comparison.

The change in ΔS for the redox process when EDTA is involved arises from two distinct contributions. First, there are changes in the configurational entropy of the ligand itself on going from a free form with many possible structural configurations to a form bound to the Cu(II) center, which has many fewer configurations. This would provide a negative entropy contribution for the oxidation process because of the many fewer states available to the complexed ligand. Second, the complexation of Cu(II) by EDTA rather than water results in the release of waters that otherwise would have been serving as ligands for Cu(II). This would provide a positive entropy contribution due to the many new states available to the free water. Together, these two effects lead to a significant change in the ΔS for the redox process when EDTA is added. For the aquo case, the net ΔS for oxidation is favorable, meaning that the ΔS is positive, giving a positive slope to the plot in Fig. 3(a). This could be interpreted as saying that the loss of order when the solid Cu metal is oxidatively dissolved outweighs the gain in order for water going from the free state to a bound, complexed state, also including the solvation shell for Cu^{2+}. In the case when EDTA is involved, the ΔS for the oxidation process becomes unfavorable (i.e., negative). This must mean that the (negative) entropy contribution from the loss of ligand configurational states outweighs the (positive) entropy contribution from the loss of the waters involved in the complexation of the Cu(II) center. This highlights the strong contributions to ΔS that arise from the large configurational density of states for the free EDTA ligand, a result of its structural flexibility. As shown in Table I, the dimerization reactions make the oxidative ΔS even more unfavorable (more negative), as expected for a process consuming three freely dissolved species (two CuEDTA complexes plus the diamine) and producing one, the dimer containing the diamine and two CuEDTA complexes. Taken together, the complexation and dimerization give a large and unfavorable entropy contribution to the free energy for oxidation, which is compared to the smaller and favorable ΔS for oxidation to the aquo species. This makes the slopes of the plots in Fig. 3(a) and Figs. 3(b)–3(d) have different signs and different magnitudes.

In order to obtain more insights on the experiments, calculations were carried out at the B3LYP/6–31 + G* level of theory using a continuum model for the solvent.[31,32] In this model, the solvent cavity is modeled as the union of a series of interlocking spheres centered on the atoms, and uses a numerical representation of the polarization of the solvent.[32] Apart from geometry optimizations of $(CuEDTA)_2(NH_2)_2(CH_2)_2{}^{4-}$ (**1**) and $(CuEDTA)_2(NH_2)_2(CH_2)_6{}^{4-}$ (**2**) complexes, the thermodynamic properties were also evaluated for several possible conformations of all the complexes. Figure 4 shows the lowest-energy structures of these complexes. In order to model the effects of the

TABLE I. Summary of calculated change in entropy at 25 °C (ΔS^{o}) and the open-circuit Seebeck coefficient (α) for Cu^{2+} (only), Cu-EDTA, its complexes, and ferro/ferricyanide thermoelectrochemical cell systems.

Electrolyte	ΔS^{o} ($\mathrm{J\ mol^{-1}\,K^{-1}}$)[a]	α (Expt.) ($\mathrm{mV\,K^{-1}}$)	α (Estim.) ($\mathrm{mV\,K^{-1}}$)[a]
$Cu + nH_2O \leftrightarrow Cu(H_2O)_n{}^{2+} + 2e^-$	+105.2	+0.57	+0.55
$Cu + EDTA^{4-} \leftrightarrow CuEDTA^{2-} + 2e-$	−217.5	−1.15	−1.13
$2CuEDTA^{2-} + (NH_2)_2(CH_2)_6 \leftrightarrow (CuEDTA)_2(NH_2)_2(CH_2)_6{}^{4-}$	−696.2	−1.50	−1.80
$2CuEDTA^{2-} + (NH_2)_2(CH_2)_2 \leftrightarrow (CuEDTA)_2(NH_2)_2(CH_2)_2{}^{4-}$	−626.1	−1.62	−1.62
$Fe(CN)_6{}^{4-} \leftrightarrow Fe(CN)_6{}^{3-} + e^-$	⋯	−1.4[b]	⋯

[a] The entropies of the EDTA complexes were obtained from Smith and Martell,[22] and the hydration entropies of Cu^{2+} ion are from Marcus and Loewenschuss.[29]

[b] Taken from Hu *et al.*[30]

change in pH on the structures and the corresponding thermodynamic properties, calculations were also carried out on the protonated species (**1H**) and (**2H**) shown in Fig. 4. The calculated Seebeck coefficients were obtained from the calculated change in entropies $\Delta S = S_{\left(\mathrm{EthyleneDiamine:CuEDTA^{2-}}\right)} - S_{(\mathrm{EthyleneDiamine})} - 2 \times S_{(\mathrm{CuEDTA^{-2}})} + 2 \times S_{\left(\mathrm{Cu^{2+}(H_2O)_4}\right)}$. Although the calculated and the experimental α are of the same order of magnitude, the calculated α of $H_2N(CH_2)_6NH_2$ and $H_2N(CH_2)_2NH_2$ complexes exhibit nearly similar values. Moreover, the protonated species (**1H**, **2H**) exhibit a slightly higher α than the non-protonated species because of the higher entropy associated with the –O–H bond. The discrepancy between the calculated and experimental Seebeck values can be due to the involvement of higher energy structures. Calculations on several conformations of the $(CuEDTA)_2(NH_2)_2(CH_2)_6{}^{4-}$ indicate that a structure, which is nearly 20 kJ mol^{-1} higher in energy, exhibits a lower α. These changes can be attributed to the modulation of the weak hydrogen bonding interaction between the acetate groups of the EDTA complex and the amino group of the diamine.

To summarize, we have used a combination of a material-by-design computational approach that allows us to scan the key design variable, the redox entropy, with a fabrication technique that harnesses the fluid nature of thermoelectrochemical cells and the potential to be inexpensively manufactured. The measurement of Seebeck coefficients in simple electrochemical systems with mixed-ligand complex formation of Cu/Cu^{+2} electrolyte suggests that these chelating ligands can improve the thermal temperature coefficient of the electrode potential (or open-circuit Seebeck coefficient) of the Cu/Cu^{2+} system up to ~185% (Fig. 5). The best case shows that control of dimerization can lead to quite large Seebeck coefficients in excess of those associated with ferro/ferricyanide cells. Continuous power generation of Cu/Cu^{2+} cells, however, will eventually oxidize the cold Cu anode. While this is a considerable inconvenience in a practical device, this can be averted by periodically reversing the hot and the cold electrodes.[18,33] Nonetheless, the ~185% enhancement of Seebeck coefficient of Cu/Cu^{2+} electrolyte will benefit copper-based thermoelectrochemical cells.[34] Its sign-reversibility will also allow the construction of thermodynamically more efficient thermoelectrochemical devices, such as a thermally regenerative electrochemical cycle (TREC), which utilizes two copper-based half-cells that have opposite signs of Seebeck coefficients, in which electrodes discharged at a low temperature can be recharged at a higher temperature.[35–37] Good agreement of the calculated and the experimental α indicates that computational strategies can be employed to design and develop a new generation of thermoelectrochemical devices with revolutionary power performance metrics based on redox couples with extremely high reaction redox entropies.

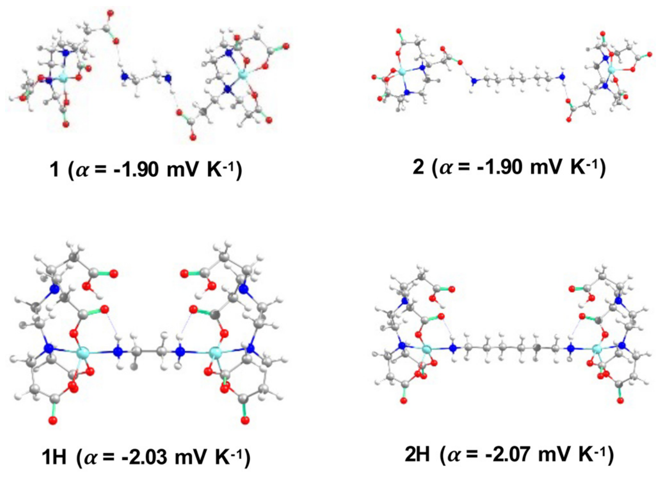
1 (α = -1.90 mV K^{-1})
2 (α = -1.90 mV K^{-1})
1H (α = -2.03 mV K^{-1})
2H (α = -2.07 mV K^{-1})

FIG. 4. B3LYP/6-31 + G* optimized conformations along with calculated Seebeck coefficient (α) of $(CuEDTA)_2(NH_2)_2(CH_2)_2{}^{4-}$ (**1**) and $(CuEDTA)_2(NH_2)_2(CH_2)_6{}^{4-}$ (**2**), and the corresponding protonated complexes (**1H**, **2H**).

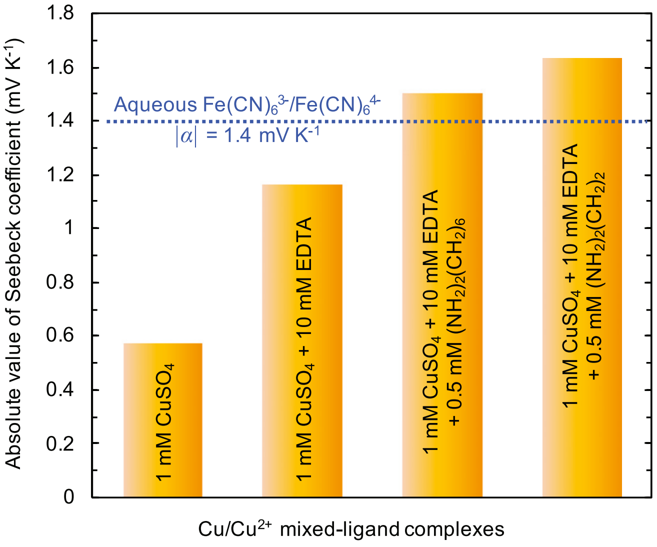

FIG. 5. Open-circuit Seebeck coefficient (absolute value) comparison between aqueous $CuSO_4$ electrolyte and its mixed-ligand complexes with EDTA, EDTA + 1,6-diaminohexane, and EDTA + 1,2-diaminoethane in thermoelectrochemical cells using Cu electrodes and 0.1 M potassium sulfate as background electrolyte.

See the supplementary material for details on pH adjustment, ionic conductivity measurements of the four studied electrolytes, and the effect of $CuSO_4$ concentration on Seebeck coefficient.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

REFERENCES

[1] B. Yu, J. Duan, H. Cong, W. Xie, R. Liu, X. Zhuang, H. Wang, B. Qi, M. Xu, Z. L. Wang, and J. Zhou, Science **370**, 342 (2020).
[2] W. Liu, X. Qian, C.-G. Han, Q. Li, and G. Chen, Appl. Phys. Lett. **118**, 020501 (2021).
[3] X. Shi and J. He, Science **371**, 343 (2021).

[4] C. G. Han, X. Qian, Q. Li, B. Deng, Y. Zhu, Z. Han, W. Zhang, W. Wang, S. P. Feng, G. Chen, and W. Liu, Science **368**, 1091 (2020).

[5] A. Gunawan, C.-H. Lin, D. A. Buttry, V. Mujica, R. A. Taylor, R. S. Prasher, and P. E. Phelan, Nanoscale Microscale Thermophys. Eng. **17**, 304 (2013).

[6] M. F. Dupont, D. R. MacFarlane, and J. M. Pringle, Chem. Commun. **53**, 6288 (2017).

[7] M. A. Buckingham, F. Marken, and L. Aldous, Sustainable Energy Fuels **2**, 2717 (2018).

[8] M. Li, M. Hong, M. Dargusch, J. Zou, and Z.-G. Chen, Trends Chem. **3**, 561 (2020).

[9] X. Wu, N. Gao, H. Jia, and Y. Wang, Chemistry **16**, 129 (2021).

[10] C. Cheng, Y. Dai, J. Yu, C. Liu, S. Wang, S. P. Feng, and M. Ni, Energy Fuels **35**, 161 (2021).

[11] J. Duan, B. Yu, L. Huang, B. Hu, M. Xu, G. Feng, and J. Zhou, Joule **5**, 768 (2021).

[12] H. Zhou, T. Yamada, and N. Kimizuka, J. Am. Chem. Soc. **138**, 10502 (2016).

[13] J. He, D. Al-Masri, D. R. MacFarlane, and J. M. Pringle, Faraday Discuss. **190**, 205 (2016).

[14] E. L. Yee, R. J. Cave, K. L. Guyer, P. D. Tyma, and M. J. Weaver, J. Am. Chem. Soc. **101**, 1131 (1979).

[15] J. T. Hupp and M. J. Weaver, Inorg. Chem. **23**, 256 (1984).

[16] J. T. Hupp and M. J. Weaver, Inorg. Chem. **23**, 3639 (1984).

[17] J. Tabib, J. T. Hupp, and M. J. Weaver, Inorg. Chem. **25**, 1916 (1986).

[18] A. Gunawan, H. Li, C.-H. Lin, D. A. Buttry, V. Mujica, R. A. Taylor, R. S. Prasher, and P. E. Phelan, Int. J. Heat Mass Transfer **78**, 423 (2014).

[19] A. Gunawan, N. W. Fette, and P. E. Phelan, in ASME 2015 Power Conference (2015).

[20] D. F. Pyreu and E. V. Kozlovskii, J. Therm. Anal. Calorim. **100**, 355 (2010).

[21] M. A. Bazanova, D. F. Pyreu, and E. V. Kozlovskii, J. Therm. Anal. Calorim. **112**, 1545 (2013).

[22] R. M. Smith and A. E. Martell, Sci. Total Environ. **64**, 125 (1987).

[23] A. J. deBethune, T. S. Licht, and N. Swendeman, J. Electrochem. Soc. **106**, 616 (1959).

[24] R. L. Magnússon, W. Kobayashi, M. Takachi, and Y. Moritomo, AIP Adv. **7**, 045002 (2017).

[25] J. J. Black, J. B. Harper, and L. Aldous, Electrochem. Commun. **86**, 153 (2018).

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

[27] R. Hu, Ph.D. thesis, University of Texas at Dallas, 2007.

[28] T. J. Kang, S. Fang, M. E. Kozlov, C. S. Haines, N. Li, Y. H. Kim, Y. Chen, and R. H. Baughman, Adv. Funct. Mater. **22**, 477 (2012).

[29] Y. Marcus and A. Loewenschuss, Annu. Rep. Prog. Chem., Sect. C **81**, 81 (1984).

[30] R. Hu, B. A. Cola, N. Haram, J. N. Barisci, S. Lee, S. Stoughton, G. Wallace, C. Too, M. Thomas, A. Gestos, M. E. Cruz, J. P. Ferraris, A. A. Zakhidov, and R. H. Baughman, Nano Lett. **10**, 838 (2010).

[31] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, A.1. ed. (Gaussian, Inc., Wallingford, CT, USA, 2009).

[32] G. Scalmani and M. J. Frisch, J. Chem. Phys. **132**, 114110 (2010).

[33] T. I. Quickenden and C. F. Vernon, Sol. Energy **36**, 63 (1986).

[34] S.-M. Jung, J. Kwon, J. Lee, K. Shim, D. Park, T. Kim, Y. H. Kim, S. J. Hwang, and Y.-T. Kim, ACS Appl. Energy Mater. **3**, 6383 (2020).

[35] S. W. Lee, Y. Yang, H. W. Lee, H. Ghasemi, D. Kraemer, G. Chen, and Y. Cui, Nat. Commun. **5**, 3942 (2014).

[36] Y. Yang, J. Loomis, H. Ghasemi, S. W. Lee, Y. J. Wang, Y. Cui, and G. Chen, Nano Lett. **14**, 6578 (2014).

[37] Y. Yang, S. W. Lee, H. Ghasemi, J. Loomis, X. Li, D. Kraemer, G. Zheng, Y. Cui, and G. Chen, Proc. Natl. Acad. Sci. U. S. A. **111**, 17011 (2014).