Tuning the Hydration Entropy of Cations during Electrochemical Intercalation for High Thermopower

Yezhou Liu, Caitian Gao, Jeonghun Yun, Yeongae Kim, Moobum Kim, Jia Li, and Seok Woo Woo Lee

A large portion of heat is wasted in the form of low-grade heat less than 100 °C. There have been various efforts to utilize such energy, such as organic ranking cycles, thermoelectrics, and thermogalvanic cells. The thermally regenerative electrochemical cycle has achieved a noticeable energy conversion efficiency of low-grade heat harvesting by the thermodynamic cycle of the electrochemical cell that the charging voltage is lower than the discharging voltage. For higher efficiency, this system requires a larger temperature coefficient (α) affected by the change of entropy of electrochemical reaction. Herein, the tuning of the hydration status of cation by mixing acetonitrile in the aqueous electrolyte to improve both negative and positive α of PBAs for highly efficient low-grade heat harvesting is presented. It largely improves α of cobalt hexacyanoferrate, which are 0.93 mV K⁻¹ at 10–30% state of charge (SOC) in 90% acetonitrile and −0.96 mV K⁻¹ at 70–90% SOC in 10% acetonitrile. A clue to understand the origin of α and to improve it further with various solvents is provided. Eventually, tuning of α using mixing solvent allows building an electrochemical cell with a large positive and negative α of electrode for highly efficient low-grade heat harvesting.

1. Introduction

Low-grade heat is an energy source in the form of thermal energy under 100 °C. Industrial waste heat, solar heat, and geothermal energy are unlimited sources of low-grade energy.² Different from solar energy and wind energy, it is still challenging to utilize low-grade heat because of the small temperature difference and low energy density.³ Thermoelectric⁴ and thermogalvanic⁵ devices, the main candidates for low-grade heat harvesting, have limited efficiency at low temperature. There had been studies of various thermodynamic cycles of electrochemical systems for low-grade heat harvesting, such as thermally regenerative electrochemical cycle (TREC), thermally regenerative ammonia battery, and copper-acetonitrile systems.⁶ The TREC uses a thermodynamic cycle of charging and discharging the electrochemical cell at alternating temperature as shown in Figure 1a.⁶ In the cycle, the thermogalvanic effect changes the output voltage of the electrochemical cell for the temperature and makes charging voltage lower than discharging voltage. This system is known to exhibit high energy conversion efficiency, but low power density compared to the other electrochemical systems. To improve power density as well as energy conversion efficiency, a temperature coefficient (α), a change of voltage for temperature, is one of the key parameters in the TREC system, because it determines how low charging voltage can be achieved compared to the discharging voltage of the cell. The electrochemical cell for TREC requires electrodes with both negative and positive α, as shown in Figure 1b. If both positive and negative electrodes have the same sign of α, their electrochemical potential changes are canceled each other, and the full cell voltage does not show meaningful change for thermal energy harvesting for change of temperature. Therefore, positive and negative electrodes must have opposite signs of α to maximize the change of full cell voltage in TREC with varying temperatures.

The α is proportional to the change of entropy of electrochemical reaction of the electrode materials as defined below.

\[ \alpha_{\text{cell}} = \frac{\partial V}{\partial T} = \frac{\Delta S}{nF} \]  

where \( V \) is the potential, \( T \) is the temperature, \( n \) is the number of electrons, \( F \) is Faraday’s constant, and \( \Delta S \) is the entropy change. There had been various demonstrations of TREC using Prussian blue analogues (PBAs) in the aqueous system using their fast kinetics and versatility for various ions.⁷ In the electrochemical reaction of PBAs, it has electrochemical intercalation of cations, which involves a change of various entropies such as entropy caused by the electrochemical oxidation of carbon-coordinated transition metal of PBA dissolved in water (\( \Delta S_{\text{aq}} \)), entropy determined by

---

DOI: 10.1002/aesr.202100176
the nitrogen-coordinated metal ions ($\Delta S_{\text{intr}}$), and entropy derived from cation transfer during the reaction ($\Delta S_{\text{ct}}$). To improve the $\alpha$ of electrode materials for highly efficient TREC using PBAs, those entropies have been modified by various methods, such as changing the transition metal of PBA and increasing the size of the cation to change the hydration status. However, these studies achieved a dramatic improvement of the negative $\alpha$, but there is a lack of studying electrode materials with positive $\alpha$.

In this article, we present the tuning of hydration status of cation by mixing acetonitrile in the aqueous electrolyte to improve both negative and positive $\alpha$ of PBAs for highly efficient low-grade heat harvesting. The electrochemical intercalation of cation into PBAs involves dehydration or partial dehydration because the size of cations is small enough to enter the framework of PBA, but the cations with the water spheres are much larger than the framework. Thus, only a few water molecules are intercalated into PBAs together as illustrated in Figure 1c. In the dehydration process, the entropy change of solvation (hydration in the case of water) of the insertion ion can present the energy change during the dehydration process. Meanwhile, the dehydration of cation induces the change of entropy ($\Delta S_{\text{ct}}$), which affects the $\alpha$. The acetonitrile molecule in the aqueous electrolyte changes the hydration status of the cation as illustrated in Figure 1c. A Raman spectroscopy study reported that metal ion is preferentially solvated by acetonitrile in the mixture of water and acetonitrile. As the acetonitrile molecule is too large to be intercalated into PBAs, the de-solvation of acetonitrile molecules changes ($\Delta S_{\text{ct}}$), and hence it changes the $\alpha$. Furthermore, controlling the concentration of acetonitrile tunes the degree of hydration of the cation, thus allowing improvement of the magnitude of both negative and positive $\alpha$ of PBAs for highly efficient low-grade heat harvesting.

To demonstrate the large negative/positive $\alpha$ of PBAs by tuning the hydration status of cation, cobalt hexacyanoferrate (CoHCFe) was used as one of the representative PBAs because it has two steps of reactions, and each reaction exhibited negative and positive $\alpha$. The first step is the reduction of Fe$^{III}$ to Fe$^{II}$, and the second step is the reduction of Co$^{III}$ to Co$^{II}$. Similar to the other PBAs, such as copper hexacyanoferrate and nickel hexacyanoferrate, the first reaction of Fe$^{III}$/Fe$^{II}$ of CoHCFe has a negative $\alpha$. In contrast, the second reaction of Co$^{III}$/Co$^{II}$ has a positive temperature. Two reaction steps have different reaction voltages and different $\alpha$.

CoHCFe nanoparticles were synthesized by co-precipitation reaction as explained in the Experimental Section. The synthesized CoHCFe is characterized by various methods as shown in Figure 2. Scanning electron microscope (SEM, JEOL FESEM 2010 HR) and X-ray diffraction (XRD, Bruker D8 Advance Powder) were used to characterize the physical property of CoHCFe. The morphology of synthesized nanoparticles is quasi-cubic, and the average size of CoHCFe nanoparticles is 100–200 nm (Figure 2a). The cubic crystal structure of CoHCFe powder is confirmed by XRD as shown in Figure 2b. Energy-dispersive X-ray spectroscopy shown in Figure 2c confirmed the existence of desired elements and even stoichiometric ratio of Fe and Co of CoHCFe.
The electrochemical performances are tested as half-cell in a three-electrode system with Ag/AgCl in 4 M KCl double junction electrode as a reference electrode. The inner solution of the reference electrode is 4 M KCl saturated with AgCl. The buffer solution in the middle layer is 1 M NaNO₃ to prevent co-precipitation of potassium ion inside and perchlorate ion in the electrolyte. The pH of the electrolyte is adjusted to 2 for the stable cycle of CoHCFe. [13]

To study the electrochemical reaction in corresponding electrolytes, cyclic voltammetry (CV) and galvanostatic cycling with potential limitations (GCPL) are tested in aqueous electrolyte and 90% acetonitrile in aqueous electrolyte for comparison. CV is in the rate of 1 mV s⁻¹. The CV curves shown in Figure 2d indicate two reaction pairs, located at 0.52/0.68 and 1.0/1.08 V for water. The formal potential of the reaction pairs are 0.6 and 1.04 V corresponding to reduction of CoIII/CoII and FeIII/FeII of CoHCFe, respectively. In 90% acetonitrile electrolyte, the CV plot of CoHCFe exhibited the same characteristic redox peaks as shown in the water. The slight increase (≈60 mV) of the formal potential of two reactions to 0.66 and 1.11 V versus standard hydrogen electrode (SHE) was caused by a change of solvation status of the cation. The potential plots versus SHE in GCPL test of CoHCFe in aqueous and 90% acetonitrile electrolyte are shown in Figure 2e when the voltage range is 0.4–1.2 V versus SHE and current density is 80 mA g⁻¹ (≈1 C). CoHCFe in 90% acetonitrile exhibited two characteristic reaction plateaus at 0.7 and 1.1 V versus SHE as CoHCFe in aqueous electrolyte does. A slight offset of the potential curve in 90% acetonitrile is also agreed with the result in the CV test. The specific capacity of CoHCFe in 90% acetonitrile electrolyte is 80 mAh g⁻¹ and the coulombic efficiency is 99.5%, which indicates stable and reversible reaction and high specific capacity as in aqueous electrolyte.

The cycling performance of CoHCFe in 25 and in 40 °C is shown in Figure 2g. CoHCFe electrode is charged and discharged in 1 M NaClO₄ in acetonitrile at a 2 C rate with activated carbon counter electrodes in 25 and 40 °C. The capacity remains 96% after 150 cycles at 25 °C, as shown in the upper blue line in Figure 2g. The average coulombic efficiency is 99.8%. The capacity remains 80% after 55 cycles at 40 °C, as shown in the upper red line in the same figure. The average coulombic efficiency is 99.8%.

The temperature coefficient (α) of CoHCFe is measured by the calculation of the slope of open circuit potential (OCP) change during temperature sweeping at the desired SOC. Figure 3a shows the potential plot of CoHCFe during discharging with constant current in electrolytes with 0%, 10%, and 90% acetonitrile. The colored circles and triangles marked on the curve indicate the condition of OCP changes for temperature presented in Figure 3b. In aqueous electrolyte (0% acetonitrile), CoHCFe exhibits positive α at lower SOC for reduction of CoIII/CoII and negative α at higher SOC for reduction of FeIII/FeII. At 30% SOC (navy circle) and 70% SOC (navy triangle), α of CoHCFe in aqueous electrolyte are 0.48 and −0.50 mV K⁻¹, respectively. In 90% acetonitrile electrolyte, α of CoHCFe at overall SOC is increased. In particular, at 30% SOC (red circle), α is increased to 0.86 mA K⁻¹. A quantity of 10% acetonitrile electrolyte induces a decrease of α at overall SOC. At 70% SOC (light blue circle), α is decreased to −0.97 mV K⁻¹.
$\alpha$ of CoHCFe for overall SOC when the concentration of acetonitrile is varied from 0% to 90% in aqueous electrolyte with 1 M NaClO$_4$. In each line, the $\alpha$ is positive at 10–40% SOC and decreases to a negative value at 60–90% SOC with the difference of around 1 mV K$^{-1}$/C$_0$. The difference between positive $\alpha$ and negative $\alpha$ is maintained for various concentrations of acetonitrile, because it is dominantly caused by the difference of $\Delta S_{\text{intr}}$ for reduction of Co$^{\text{III}}$/Co$^{\text{II}}$ at lower SOC and of Fe$^{\text{III}}$/Fe$^{\text{II}}$ at higher SOC of CoHCFe, which is independent of the solvation status of cation.\textsuperscript{[13]} The lines in different colors refer to different concentrations of acetonitrile. Acetonitrile concentrations of 30, 50, 70, and 90% are in the tendency of a linear positive offset. But from 0% to 10% of acetonitrile concentration, the $\alpha$ has a sudden drop-down of 0.75 mV K$^{-1}$. This tendency is clearly exhibited in Figure 3d. A quantity of 30% SOD (black line) and 70% SOD (red line) are selected to show the tendency of $\alpha$ for the concentrations of acetonitrile in the electrolyte and the difference of $\alpha$ between two reactions corresponding to the reduction of Co$^{\text{III}}$/Co$^{\text{II}}$ and of Fe$^{\text{III}}$/Fe$^{\text{II}}$. The offset of $\alpha$ for the concentration of acetonitrile without change of tendency for SOC explains that change of hydration status of cation affects $\Delta S_{\text{intr}}$ while $\Delta S_{\text{intr}}$ is not.

Copper hexacyanoferrate (CuHCFe) is one of the well-known PBAs used for energy storage and conversion applications.\textsuperscript{[14]} We have investigated its temperature coefficient ($\alpha$) change for the concentration of acetonitrile in water with 1 M NaClO$_4$. Each line, the $\alpha$ is positive at 10–40% SOC and decreases to a negative value at 60–90% SOC with the difference of around 1 mV K$^{-1}$ according to the two reactions of CoHCFe in sodium ion electrolyte. The difference between positive $\alpha$ and negative $\alpha$ is maintained for various concentrations of acetonitrile, because it is dominantly caused by the difference of $\Delta S_{\text{intr}}$ for reduction of Co$^{\text{III}}$/Co$^{\text{II}}$ at lower SOC and of Fe$^{\text{III}}$/Fe$^{\text{II}}$ at higher SOC of CoHCFe, which is independent of the solvation status of cation.\textsuperscript{[13]} The lines in different colors refer to different concentrations of acetonitrile. Acetonitrile concentrations of 30, 50, 70, and 90% are in the tendency of a linear positive offset. But from 0% to 10% of acetonitrile concentration, the $\alpha$ has a sudden drop-down of 0.75 mV K$^{-1}$. This tendency is clearly exhibited in Figure 3d. A quantity of 30% SOD (black line) and 70% SOD (red line) are selected to show the tendency of $\alpha$ for the concentrations of acetonitrile in the electrolyte and the difference of $\alpha$ between two reactions corresponding to the reduction of Co$^{\text{III}}$/Co$^{\text{II}}$ and of Fe$^{\text{III}}$/Fe$^{\text{II}}$. The offset of $\alpha$ for the concentration of acetonitrile without change of tendency for SOC explains that change of hydration status of cation affects $\Delta S_{\text{intr}}$ while $\Delta S_{\text{intr}}$ is not.

Figure 3. The temperature coefficient ($\alpha$) of CoHCFe in 1 M NaClO$_4$ in the mixture of acetonitrile and water for various concentrations of acetonitrile.

(a) Discharging plot of CoHCFe for 0%, 10%, and 90% of acetonitrile in water. (b) OCP change for temperature compared to the initial OCP at 10 °C and $\alpha$ at 30% and 70% SOC for three concentrations of acetonitrile indicated by colored circles and triangles in a). (c) Mapping of $\alpha$ for SOC and concentration of acetonitrile. (d) $\alpha$ For the concentration of acetonitrile at 30% and 70% SOC.

$\alpha$ of CoHCFe for overall SOC when the concentration of acetonitrile is varied from 0% to 90% in aqueous electrolyte with 1 M NaClO$_4$. Each line, the $\alpha$ is positive at 10–40% SOC and decreases to a negative value at 60–90% SOC with the difference of around 1 mV K$^{-1}$ according to the two reactions of CoHCFe in sodium ion electrolyte. The difference between positive $\alpha$ and negative $\alpha$ is maintained for various concentrations of acetonitrile, because it is dominantly caused by the difference of $\Delta S_{\text{intr}}$ for reduction of Co$^{\text{III}}$/Co$^{\text{II}}$ at lower SOC and of Fe$^{\text{III}}$/Fe$^{\text{II}}$ at higher SOC of CoHCFe, which is independent of the solvation status of cation.\textsuperscript{[13]} The lines in different colors refer to different concentrations of acetonitrile. Acetonitrile concentrations of 30, 50, 70, and 90% are in the tendency of a linear positive offset. But from 0% to 10% of acetonitrile concentration, the $\alpha$ has a sudden drop-down of 0.75 mV K$^{-1}$. This tendency is clearly exhibited in Figure 3d. A quantity of 30% SOD (black line) and 70% SOD (red line) are selected to show the tendency of $\alpha$ for the concentrations of acetonitrile in the electrolyte and the difference of $\alpha$ between two reactions corresponding to the reduction of Co$^{\text{III}}$/Co$^{\text{II}}$ and of Fe$^{\text{III}}$/Fe$^{\text{II}}$. The offset of $\alpha$ for the concentration of acetonitrile without change of tendency for SOC explains that change of hydration status of cation affects $\Delta S_{\text{intr}}$ while $\Delta S_{\text{intr}}$ is not.

Copper hexacyanoferrate (CuHCFe) is one of the well-known PBAs used for energy storage and conversion applications.\textsuperscript{[14]} We have investigated its temperature coefficient ($\alpha$) change for the concentration of acetonitrile in water with 1 M NaClO$_4$ to compare with the aforementioned behavior of CoHCFe. To confirm the proper reaction of CuHCFe in acetonitrile and water mixture, GCPL at about 1 C rate was tested in 0%, 10%, and 50% of acetonitrile in water. All GCPL plots exhibit a single plateau and similar specific capacity between 53.6 and 56.5 mAh g$^{-1}$ as shown in Figure 4a. When acetonitrile is mixed in the aqueous electrolyte, offset of the potential curve is occurred because the presence of acetonitrile causes the change of hydrated status of cation to be intercalated into PBAs with dehydration. The mapping of $\alpha$ of CuHCFe for SOC is plotted when the concentration of acetonitrile in the aqueous electrolyte is increased from 0% to 50%, as shown in Figure 4b. As previous studies of CuHCFe presented, $\alpha$ of CuHCFe does not vary significantly for SOC.\textsuperscript{[13]} However, $\alpha$ exhibited a clear shift for the concentration of acetonitrile as observed in the test of CoHCFe. The average $\alpha$ in the whole range of SOC in Figure 4c shows this tendency more clearly. The coefficient is $-0.661$ mV K$^{-1}$ in pure aqueous electrolyte and increased to $-0.432$ mV K$^{-1}$ in 10% acetonitrile. Then, it is gradually decreased to $-0.621$ mV K$^{-1}$ in 50% acetonitrile. As observed in CoHCFe, CuHCFe also exhibited a shift of $\alpha$ upon the presence of acetonitrile, changing the hydration status of cation, and the degree of shift is affected by the concentration of acetonitrile in aqueous electrolyte.

2. Conclusion

We have demonstrated improvement in the magnitude of both positive and negative $\alpha$ of PBAs by tuning the hydration status of cation for highly efficient low-grade heat harvesting. Acetonitrile mixed in aqueous electrolyte changes the hydration status of
cation and tunes the change of entropy for dehydration process ($\Delta S_D$) upon electrochemical intercalation into PBAs. Furthermore, varying the concentration of acetonitrile allows versatile tuning of $\alpha$ upward or downward of PBAs. Therefore, it achieved largely improved $\alpha$ of CoHCFe, which are 0.93 mV K$^{-1}$ at 10–30% SOC in 90% acetonitrile and $-0.96$ mV K$^{-1}$ at 70–90% SOC in 10% acetonitrile. Both large positive and negative $\alpha$ of the electrode could make large $\alpha$ of the full cell for highly efficient low-grade heat. To build the TREC system, 10–30% of SOC and 70–90% of SOC of CoHCFe can be used as an anode and a cathode of the full cell to provide the opposite sign of $\alpha$ with an ion exchange membrane to separate the electrolyte of different concentrations of acetonitrile. Furthermore, each SOC of CoHCFe can make a pair with other counter electrodes with opposite signs of $\alpha$ to build a full cell. Large offset of $\alpha$ is also observed in CuHCFe, another PBA. This large offset of $\alpha$ by mixing solvents provides a new fundamental understanding of $\alpha$ that the hydration status of cation and its dehydration process into PBAs are playing an important role. Although we have tested acetonitrile, one of the common solvents in this study, further study of tuning the hydration (or solvation) status of the cation with various solvents will improve $\alpha$ of electrochemical cells for highly efficient heat conversion.

3. Experimental Section

Synthesis of CoHCFe Nanoparticle: A quantity of 60 mL of 40 mM Co(NO$_3$)$_2$ and 60 mL of 20 mM K$_3$Fe(CN)$_6$ were dissolved in deionized water. A quantity of 30 mL of deionized water was prepared in a 500 mL beaker and put on the surface of a hot plate. A stirring bar was settled in the beaker with the speed of 400 RPM, and a thermometer was fixed in the beaker to monitor the temperature as 40 °C. Then, these two solutions were dropped at the speed of 0.3 mL s$^{-1}$ into the beaker. The color of the solution became green. After aging for a night, the CoHCFe powder was separated from water and washed by deionized water twice, and washed by acetonitrile twice in a centrifuge to remove the ions on the surface. Then, the powder of CoHCFe was dried in a vacuum oven at 100 °C for a night. Finally, the green color CoHCFe powder was synthesized.

Fabrication of CoHCFe Electrode: CoHCFe electrodes were prepared by the same method: 80% wt/wt CoHCFe, 10% wt/wt carbon black, and 10% wt/wt PVDF were added into NMP and mixed as slurry. Then, the slurry was pasted on one side of 4 cm$^2$ carbon cloth. The electrodes were dried in a vacuum oven at 100 °C for a night. The mass of CoCHFe on the carbon cloth was about 4 mg.

Figure 4. The temperature coefficient ($\alpha$) of CuHCFe in 1 M NaClO$_4$ in the mixture of acetonitrile and water for various concentrations of acetonitrile. a) GCPPL plot of CoHCFe for 0%, 10%, and 50% of acetonitrile in water. b) Mapping of $\alpha$ for SOC and concentration of acetonitrile. c) Average $\alpha$ in the whole range of SOC for the concentration of acetonitrile at 50% SOC.

Electrochemical Cell Configuration and Test: Three-electrode flooded cell was used for electrochemical characterization and TREC test. The working electrode was CoHCFe on the carbon cloth. The counter electrode was a large amount of activated carbon on carbon cloth. The reference electrode was Ag/AgCl in 4 M KCl solution. The electrochemical characterization was done by a multichannel potentiostat (VMP3, Bio-logic). The temperature of the cell was controlled by an environment chamber (MK56, Binder).

Acknowledgements

S.W.L. acknowledges the support by Academic Research Fund Tier 2 from Ministry of Education, Singapore, under ref. no. MOE2019-T2-1-122.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Y.L. and S.W.L. conceived the idea and designed the experiment. Y.L. performed the overall experiments. C.G. assisted characterization of the materials. J.Y., Y.K., M.K., and J.L. provided technical and scientific advice. Y.L. and S.W.L. wrote the manuscript, and all authors provided feedback on it.

Data Availability Statement

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

Keywords

electrochemical systems, hydration, intercalation, low-grade heat harvesting, Prussian blue analogues

Received: October 31, 2021
Revised: December 4, 2021
Published online: January 5, 2022

[1] C. Chan, J. Ling-Chin, A. Roskilly, Appl. Therm. Eng. 2013, 53, 160.
[2] B. F. Tchanche, G. Lambrinos, A. Frangoudakis, G. Papadakis, Renewable Sustainable Energy Rev. 2011, 15, 3963.
[3] a) F. D. Rosi, *Solid-State Electron.* 1968, 11, 833; b) G. J. Snyder, E. S. Toberer, *Nat. Mater.* 2008, 7, 105; c) B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. Liu, M. S. Dresselhaus, G. Chen, Z. Ren, *Science* 2008, 320, 634; d) L. E. Bell, *Science* 2008, 321, 1457.

[4] a) A. Gunawan, C.-H. Lin, D. A. Buttry, V. Mujica, R. A. Taylor, R. S. Prasher, P. E. Phelan, *Nanoscale Microscale Thermophys. Eng.* 2013, 17, 304; b) T. I. Quickenden, Y. Mua, *J. Electrochem. Soc.* 1995, 142, 3985; c) R. Hu, B. A. Cola, N. Haram, J. N. Barisci, R. H. Baughman, *Nano Lett.* 2010, 10, 838; d) P. F. Salazar, S. Lee, S. Stoughton, G. Wallace, C. Too, M. Thomas, A. Gestos, M. E. dela Cruz, J. P. Ferraris, A. A. Zakhidov, *J. Electrochem. Soc.* 2012, 159, B483; e) N. S. Hudak, G. G. Amatucci, *J. Electrochem. Soc.* 2011, 158, A572.

[5] a) D. Brogioli, F. La Mantia, *Energy Environ. Sci.* 2021, 14, 1057; b) R. Springer, N. R. Cross, S. N. Lvov, B. E. Logan, C. A. Gorski, D. M. Hall, *J. Electrochem. Soc.* 2021, 168, 070523.

[6] a) R. Long, B. D. Li, Z. C. Liu, W. Liu, *Energy* 2015, 87, 463; b) C. T. Gao, S. W. Lee, Y. Yang, *ACS Energy Lett.* 2017, 2, 2326; c) X. Zhu, M. Rahimi, C. A. Gorski, B. Logan, *ChemSusChem* 2016, 9, 873; d) S. W. Lee, Y. Yang, H. W. Lee, H. Ghasemi, D. Kraemer, G. Chen, Y. Cui, *Nat. Commun.* 2014, 5, 3942.

[7] a) C. Gao, Y. Yin, L. Zheng, Y. Liu, S. Sim, Y. He, C. Zhu, Z. Liu, H. W. Lee, Q. Yuan, *Adv. Funct. Mater.* 2018, 28, 1803129; b) S. W. Lee, Y. Yang, H.-W. Lee, H. Ghasemi, D. Kraemer, G. Chen, Y. Cui, *Nat. Commun.* 2014, 5, 3942; c) Y. Liu, C. Gao, S. Sim, M. Kim, S. W. Lee, *Chem. Mater.* 2019, 31, 4379.

[8] F. Scholz, A. Dostal, *Angew. Chem., Int. Ed.* 1995, 34, 2685.

[9] a) C. Gao, Y. Yin, L. Zheng, Y. Liu, S. Sim, Y. He, C. Zhu, Z. Liu, H. W. Lee, Q. Yuan, *Adv. Funct. Mater.* 2018, 28, 1803129; b) C. Gao, Y. Liu, B. Chen, J. Yun, E. Feng, Y. Kim, M. Kim, A. Choi, H.-W. Lee, S. W. Lee, *Adv. Mater.* 2021, 33, 2004717.

[10] H.-W. Lee, M. Pasta, R. Y. Wang, R. Ruffo, Y. Cui, *Faraday Discuss.* 2015, 176, 69.

[11] a) Y. Reynier, J. Graetz, T. Swan-Wood, P. Rez, R. Yazami, B. Fultz, *Phys. Rev. B* 2004, 70, 174304; b) D. Spångberg, *Acta Univ. Ups.* 2003; c) H.-W. Lee, M. Pasta, R. Y. Wang, R. Ruffo, Y. Cui, *Faraday Discuss.* 2015, 176, 69; d) J. Newsome, G. Neilson, J. Enderby, M. Sandström, *Chem. Phys. Lett.* 1981, 82, 399.

[12] B. G. Oliver, G. J. Janz, *J. Phys. Chem.* 1970, 74, 3819.

[13] C. Gao, Y. Yin, L. Zheng, Y. Liu, S. Sim, Y. He, C. Zhu, Z. Liu, H. W. Lee, Q. Yuan, *Adv. Funct. Mater.* 2018, 28, 1803129.

[14] a) J. Yun, Y. Zeng, M. Kim, C. Gao, Y. Kim, L. Lu, T.-H. Kim, W. Zhao, T.-H. Bae, S. W. Lee, *Nano Lett.* 2021, 21, 1659; b) C. D. Wessells, R. A. Huggins, Y. Cui, *Nat. Commun.* 2011, 2, 550; c) I. D. Jung, M. Kim, C. Gao, Y. Liu, C. Park, H.-W. Lee, S. W. Lee, *Nano Lett.* 2020, 20, 1800.