Proceedings of the joint 16th International Green Energy Conference (IGEC-XVI)
& 5th International Conference on Energy and AI (ICEAI-V)
& Symposium on Chemical Engineering and AI
IGEC2024-911~915 (invited)
June 30 - July 4, 2024, Ningbo, China

Special Session: New electrochemical systems for low-grade heat recovery

Session Description:

A large amount of heat is at the temperature of <100 °C, which is estimated to be around 60% of the total waste heat. The exploitation of such sources would benefit for the improvement of energy efficiency and the reduction of carbon footprint. How to efficiently convert such energy into electricity is a big challenge as the heat sources are typically distributed and exhibit narrow temperature difference with the ambient. Traditional technologies such as organic Rankine cycles and solid-state thermoelectric generators are being actively pursued but face their challenges in efficiency, cost, and system complexity.

This Special Session provides a unique platform to present state-of-the-art research findings in heat-to-electricity techniques from such low-temperature heat sources, especially the emerging technologies based on the electrochemical working principles. Contributions regarding the material exploration, device development and system operation, from experiment to theoretical modeling, are welcomed.

Session Organizer(s):

Xiaoya Li (Shanghai Jiao Tong University)

Zhi Li (Zhejiang University)

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Topic 2: Heat/mass coupling transfer analysis and optimization of thermocells driven by low-grade heat
Topic 3: Electrochemical Brayton cycle: A new approach to utilizing low and medium grade thermal energy
Topic 4: Selective tuning the thermopower of ionic thermoelectrics for low-grade heat harvesting
Topic 5: Entropy change regulation in thermally regenerative electrochemical cycles

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Topic 1: Explore the low-grade heat harvesting in divalent ion batteries

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Abstract: Thermally regenerative electrochemical cycle (TREC), whose energy conversion efficiency largely depends on the temperature coefficient of the electrode material, shows promising for low-grade heat (<100 °C) harvesting. In particular, a high-temperature coefficient will require a significant change of hydration entropy of ion hosting materials, which can be tuned by electrolyte concentration, charge state, and radius of intercalated ions. Previous research mainly focused on studying the intercalation of monovalent cations with electrode material for the TREC system. Here, we explored the effect of the electrochemical intercalation of divalent cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) on the hydration entropy in copper hexacyanoferrate (CuHCFe). A high-temperature coefficient of -0.711 mV K^{-1} in the Mg ion system due to its higher ionic potential, which causes a more significant change in the hydration entropy. We further show that the lattice parameter has a remarkable shrinkage ratio during Mg ion intercalation, indicating a significant negative temperature coefficient. This work will provide insight into the change entropy during electrochemical intercalation and further guide the design of the efficient TREC system for low-grade heat harvesting.

Keywords: Low-grade heat harvesting; Thermally regenerative electrochemical cycle; Multi-valent cations; Temperature coefficient

Dr. Caitian Gao graduated from Lanzhou University in 2015, and she worked as a research fellow at Nanyang Technological University from 2016 to 2021. Now she is an associate professor at School of Physics and Electronics in Hunan University. The main research activities for Dr. Gao include energy conversion devices for solar or thermal energy conversion, and energy storage batteries, like alkaline metal batteries. In particular, she focuses on studying the temperature effect on electrochemical systems, developing high-efficient thermally regenerative electrochemical cycle for low-grade heat harvesting and high-performance low-temperature energy storage systems. Dr. Gao has published 62 research papers, including *Nature Communication, Advanced Materials, Angewandte Chemie, ACS Energy Letter, Advanced Functional Materials* etc. The total citation is over 4500 and H index is 34.

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Topic 2: Heat/mass coupling transfer analysis and optimization of thermocells driven by low-grade heat

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Abstract: As a cutting-edge heat-to-electricity technology, thermocells possess the advantages of large Seebeck coefficient, low cost and high scalability, indicating a great prospect in low-grade heat recovery. Most studies about thermocells have conducted by experiments to explore the effects of electrode and electrolyte materials, while very few simulation studies were reported before, leading to the unclear mechanism of heat/mass coupling transfer process. This study aims to reveal the effects of different operating parameters on the thermocell performance by simulation. Firstly, a multi-physical model considering the diffusion, migration and convection process will be established. Then the effects of key operating parameters including the electrode temperature, electrode distance and electrode orientation will be evaluated on the thermocell performance, clarifying the restrictions to the ion transport process. Finally, performance enhancement method will be proposed to relieve the restriction factors and improve the performance of thermocells, providing design and optimization guidelines for future development of thermocells.

Keywords: thermocells, thermal energy conversion, low-grade heat recovery, multi-physical model

Dr. Zhi Li is now working as an associate research professor in the College of Energy Engineering at Zhejiang University (ZJU). He obtained his Doctor of Engineering from ZJU (2021), and his PhD thesis is awarded as the annual excellent thesis of the ZJU (Top 5%). He also completed a postdoctoral fellowship in the College of Energy Engineering at ZJU (2024). Dr. Li focuses on fundamental and application research on waste heat recovery, thermal energy storage and their coupling in distributed energy systems. His research is funded by the National Natural Science Foundation of China (NSFC) and other highly prestigious enterprises. To date, Dr. Li has published over 20 SCI-indexed journal articles (First and corresponding authors) on *Applied Energy, Energy Conversion and Management, Energy* etc.

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Topic 3: Electrochemical Brayton cycle: A new approach to utilizing low and medium grade thermal energy

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Abstract: Efficient technologies to convert huge amounts of low-grade heat to power are urgently desired. Although various electrochemical technologies have been proposed, the low thermal efficiency and power density still limit their practical applications. Starting from the ideal cycle of thermo-chemical engines and the decoupling of heat transfer and charge transport, we have proposed the electrochemical Brayton cycle (EBC) for power generation, which is realized by flow batteries and heat exchangers. By establishing energy and entropy generation models, the thermal efficiency and power density of ideal and actual EBC systems, as well as the isentropic efficiency and entropy generation are analyzed and discussed. A small principal prototype was built and subjected to long-term performance testing. The results indicate the ideal EBC without overpotential performs a maximum power density of 690 W m^{-2} and a relative efficiency to Carnot efficiency of 52.3% when operated between 25 and 75 °C. With 70% heat regeneration, the relative efficiency and power density of actual EBC could reach 45.3% and 1.6 W m^{-2}. Further entropy generation analysis reveals that the main contributors to entropy generation are heat transfer, activation overpotential and ohmic overpotential in order of magnitude. Furthermore, the high efficiency of EBC compared with other technologies, its broad application space, especially its advantages of integration with energy storage indicate its feasibility and potential.

Keywords: Thermodynamic cycle, Electrochemical cycle, low and medium grade thermal energy, energy efficiency

Dr. Xu Weicong, received his PhD degree from Tianjin University in 2021, is now an assistant researcher at the State Key Laboratory of Engines at Tianjin University. He visited University of California, Berkeley from 2019 to 2020. His main research is advanced energy conversion and storage technology based on advanced thermal cycle and thermo-electrochemical cycle. He has published over 30 papers and received special and general funding from the China Postdoctoral Fund. He won the second prize of Science and Technology from the Chinese Society of Engineering Thermo-physics and the first prize of Science and Technology from the Tianjin Renewable Energy Society.

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Topic 4: Selective tuning the thermopower of ionic thermoelectrics for low-grade heat harvesting

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Abstract: Thermal energy is a highly abundant resource in nature, accounting for nearly half of all energy consumption. There is a pressing need to develop effective technologies that can harness the vast thermal resources available for power generation. Electronic thermoelectric (e-TE) devices have been instrumental in converting heat into useful electricity, but they suffer from low Seebeck coefficient (μVK^{-1}), high cost, and toxicity, making it challenging to generate sufficient voltages for practical applications. Recently, ionic thermoelectric (i-TE) polymer materials have indeed gained significant interest in recent years, demonstrating remarkable advancements by exhibiting giant Seebeck coefficients of millivolts per kelvin ($mV\ K^{-1}$). These materials utilize ions as energy carriers, which is a unique feature distinguishing them from traditional thermoelectric materials that primarily rely on electrons. However, the current state-of-the-art ionic thermoelectric materials face substantial hurdles when it comes to producing consistent power output over extended periods and suffer from the absence of N-type variants. These drawbacks pose constraints on the broader integration of i-TE technology into tangible applications in thermoelectric power generation. This topic introduces an all-solid-state PVDF-HFP/NaTFSI/PC with high thermopower of +20 $mV\ K^{-1}$ is successfully developed and the p-n conversion from +20 to −6 $mV\ K^{-1}$ is achieved by doping a certain amount of (pentafluorophenyl)boron (TPFPB) with highly electronegativity negative property. Meanwhile, the mechanism of p-n conversion is studied in detail based on the analysis of the changes in polymer structure, ion transport as well as Eastman entropy. Furthermore, a reversible bipolar thermopower behavior of the same PVDF-HFP/NaTFSI/PC material by adjusting ion-electrode interactions is found and exhibits giant p-type (+20 $mV\ K^{-1}$) and n-type (−10.2 $mV\ K^{-1}$) thermopower, respectively. By utilizing the bipolar thermopower property, an ionic thermoelectric generator is developed and can produce cyclic energy under a constant heat condition.

Keywords: Ionic-thermoelectrics, P-N conversion, thermodiffusion, heat harvesting

Dr. Cheng Chi is an associate professor in School of Energy and Power Engineering at North China Electric Power University. He obtained a Bachelor of Engineering from the South China University of Technology (2012) and obtained a Master (2015) and Ph.D. (2019) degree in Mechanical Engineering from the Hong Kong University of Science and Technology. He also completed a postdoctoral fellowship in School of Aerospace at Tsinghua University (2022). Dr. Chi is dedicated to the research of heat transfer, ionic thermoelectric, and thermogalvanic, energy storage materials and devices for the recovery and utilization of low-grade thermal energy. Currently, he is leading projects such as the National Natural Science Foundation of China, etc. He has been awarded the 9th "Young Elite Scientists Sponsorship Program" of the Chinese Society for Electrical Engineering (2023-2025), the Outstanding Postdoctoral Fellows at Tsinghua University in 2022. Dr. Chi has published over 20 SCI-indexed academic papers in high-impact journals such as Nature Communications (2 articles).

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Topic 5: Entropy change regulation in thermally regenerative electrochemical cycles

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Abstract: Low-grade thermal energy harvesting is significant for energy efficiency improvement. Among various technologies, the thermally regenerative electrochemical cycle (TREC) has been demonstrated to exhibit a high theoretical efficiency. TREC uses the temperature dependence of electrochemical cell voltage and construct a thermodynamic cycle for direct heat-to-electricity conversion. The capability of such temperature dependence is characterized by the temperature coefficient, which depends on the entropy change during the electrochemical reaction. A higher entropy change can result in a larger voltage difference and more electricity generation. Here, we found that the counterions in the electrolyte also have an impact on the temperature coefficient. The noncoordinating chaotropic anion enables higher entropy change than the kosmotropic anions. It is attributed to the variation of the desolvation and reorganization entropy changes during the redox reaction. Leveraging this finding, we demonstrate a TREC system with a CuHCFe cathode, Fe^{2+}/Fe^{3+} anode, and $NaClO_4$ electrolytes, which achieved a full-cell α of −3.040 mV K^{-1} and the energy efficiency of 4.1% (27% of the Carnot efficiency) when the cell operates between 10 and 60 °C without heat recuperation. This work gives insight into enhancing entropy change by tailored counterions.

Keywords: Thermally regenerative electrochemical cycle, temperature coefficient, coordinating nature of anions

Dr. Xiaoya Li received her Ph. D. degree in Mechanical Engineering from Tianjin University in 2020. She is currently a tenure-track associate professor in School of Mechanical Engineering, Shanghai Jiao Tong University. Prior to that, she was a research fellow in School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore. She visited Imperial College London and Ghent University from 2018 to 2019. Her research interests are intelligent design and advanced control for vehicles, vehicle thermal management and high-performance energy harvesting and storage technologies. Dr. Li has published over 40 research papers, including *ACS Energy Letters, Nano Energy, Applied Energy*, etc.