

International Workshop on Thermo-electrochemical Devices 2023

(7-8 September 2023, Benicàssim, Spain)

Book of abstracts



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Programme

Thursday, 7th September	
8:30 - 9 h	Registration (entrance of the conference room)
9 - 9:15 h	Opening and welcome
Session 1: Thermocells	
9:15 - 10 h	Invited talk: Leigh Aldous , S. Hammoud, M. A. Troshova, M. A. Buckingham (King's College London, United Kingdom) Thermogalvanic cells: The role of redox active ion concentration, ratio, solvent and measurement conditions upon power and genuine efficiency
10 - 10:20 h	Tepei Yamada , H. Zhou (The University of Tokyo, Japan) Proton-coupled electron transfer reaction for smart thermocells
10:20 - 10:40 h	Sergio Castro-Ruiz , J. García-Cañadas (Universitat Jaume I, Spain) Investigation of the performance of a nanostructured and porous Sb-doped tin oxide electrode in a thermo-electrochemical cell
10:40 - 11 h	S. Caramori , L. Vesce, A. Di Carlo, E. Marchini, S. Carli, Andrea Reale (University of Ferrara, Italy) Thermoelectrochemical redox systems for low temperature grade energy harvesting
11 - 11:30 h	Coffee break
Session 2: Thermocells	
11:30 - 12:15 h	Invited talk: Sawako Nakamae (CEA, CNRS, Université Paris Saclay, France) Thermoelectricity in nanofluids: Is there a future?
12:15 - 12:35 h	Qingshuo Wei , S. Horike, M. Mukaida, K. Kirihara, K. Seki (National Institute of Advanced Industrial Science and Technology (AIST), Japan) Study of thermocells using ferricyanide/ferrocyanide and their application to self-powered sensors
12:35 h - 12:55 h	I. Giannoutsos, M. Beaughon, T. Salez, T. Fiuza, Sawako Nakamae , S. Bouguila, V. Slakov, V. Zinovyeva (CEA, CNRS, Université Paris Saclay, France) Thermogalvanic energy conversion improvement in ionic liquids: redox solvation and coordination chemistry
12:55 - 13:15 h	Oscar J. Dura , C. Martín, A. López-Hazas, S. Merino, E. Vázquez (Universidad de Castilla-La Mancha, Instituto Regional de Investigación Científica Aplicada, Spain) Soft thermoelectric materials based on hydrogels
13:15 - 14:45 h	Lunch
Session 3: Ionic thermoelectric supercapacitors	
14:45 - 15:30 h	Invited talk: Xavier Crispin (Linköping University, Sweden) Ionic thermoelectric supercapacitors
15:30 - 15:50 h	Weishu Liu (Southern University of Science and Technology, China) Gelatin-based ionic thermoelectric gel for energy harvesting
15:50 - 16:10 h	Mario Culebras , M. Muddasar, N. Menendez, A. Quero, M. Collins, C. Gómez (Universitat de València, Spain) Lignin-derived ionic thermoelectric hydrogels for low-grade thermal energy

	harvesting
16:10 - 16:30 h	<u>Ievgen Nedrygailov</u> , K. Rahme, S. Monaghan, S. Biswas, P. Hurley, J. D. Holmes (University College Cork, Ireland) Nanowood: Fully renewable, biodegradable, environmentally friendly, natural material for the next generation thermoelectrics
16:30 - 17 h	Coffee break
17 - 18 h	Posters session
20:30 h	Gala dinner at Rebois de Roures (departure from the venue at 20 h)
Friday, 8th September	
Session 4: Thermocells/Other thermo-electrochemical devices	
8:55 - 9:40 h	Invited talk: <u>Hongyao Zhou</u> , T. Yamada (The University of Tokyo, Japan) Increasing the entropy change in thermocells by intermolecular forces
9:40 - 10 h	<u>Rajkumar Sarma</u> , S. Hardt (<u>TU Darmstadt, Germany</u>) Thermovoltage generation with thermally activated electrolytes
10 - 10:20 h	Doriano Brogioli (Universität Bremen, Germany) Performance parameters for ranking the techniques for low-temperature heat exploitation
10:20 - 10:40 h	Heiko Reith , A. S. Dutt, V. Barati, N. B. Pulumati, K. Nielsch (Leibniz Institute of Solid State and Materials Research, TU Dresden, Germany) Thermoelectric characterization of electrodeposited materials and its application in micro-thermoelectric devices
10:40 - 11 h	Nithin B. Pulumati , A. S. Dutt, D. Berger, N. Sherkat, U. Pelz, P. Woias, K. Nielsch, H. Reith (Leibniz Institute of Solid State and Materials Research, TU Dresden, Germany) Height optimized micro-thermoelectric devices
11 - 11:30 h	Coffee break
11:30 - 11:50 h	Mauricio Solis-de la Fuente , S. Castro-Ruiz, L. Márquez-García, P. Rullière, S. Fantini, R. del Olmo, N. Casado, J. García-Cañadas (Universitat Jaume I, Spain) Large increase in the electrical conductivity with small change in the Seebeck coefficient for a nanostructured and porous oxide in contact with a solid electrolyte
11:50 - 12:50 h	Open discussion of controversial topics
12:50 - 13 h	Closing and farewell
13 h	Lunch
<i>Legend: Underlined speaker with a double line and in blue means on-line talk. Talk with institution underlined with a dotted line and in red means that its recording will not be available.</i>	

Posters

Poster contributions (Thursday, 7th September, 17-18 h)	
Thermocells	
1	<u>P. Santos Candiotto de Oliveira</u> , D. Zhao, Z. U. Khan, X. Crispin (Linköping University, Sweden) Printed p-n type Thermogalvanic Modules for Energy Conversion
2	<u>W. Zhang</u> , M. Cerro, A. de Andrés, L. Velasco, M. Sauvan, D. Moonshiram, M. C. Gutiérrez, F. del Monte, M. L. Ferrer (Instituto de Ciencia de Materiales de Madrid, CSIC, Spain) Thermoelectrics based on Fe liquid mixtures
3	<u>H. Inoue</u> , S. Nakagawa, Z. Hongyao, H. Ando, T. Yamada (The University of Tokyo, Japan) All-organic thermocell with high Seebeck coefficient achieved by the formation of local solvation cage based on hydrogen bond
Ionic thermoelectric supercapacitors	
4	<u>S. Horike</u> , Q. Wei, K. Kirihara, M. Mukaida, T. Sasaki, Y. Koshiba, K. Ishida (Kobe University, Japan) Thermally chargeable supercapacitor based on ionic hydrogels with tunable polarity
5	N. M. Menéndez, R. Muñoz-Espí, A. Cantarero, M. Culebras, <u>C. M. Gómez</u> (Universitat de València, Spain) Thermoelectric properties of ionic materials derived from lignocellulosic biomass residue
<i>All posters will be presented in-person by the author in bold underlined.</i>	

Oral contributions

Topic:

Thermo-electrochemical cells (thermocells or thermogalvanic cells)

Thermogalvanic cells: The role of redox active ion concentration, ratio, solvent and measurement conditions upon power and genuine efficiency

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Given the vast quantities of under-utilised low-grade waste heat, thermogalvanic thermocells (or thermoelectrochemical devices) are receiving increasing attention. They demonstrate promising ability to convert a temperature gradient into a flow of electrical current, and at their most simple can comprise of two electrodes, water and a compound in two redox states [1]. Entropy and temperature difference between the redox states largely dictates the devices' voltage [2], while the current is influenced by a larger number of factors [1,2,3]. Since simple molecular diffusion are the only moving parts, it means in theory the devices can operate for extended periods of time.

This talk will summarise recent fundamental investigations into thermogalvanic cells. Briefly, the concentration of the redox species [2,3], the ratio of the oxidised:reduced species [2] and ionic strength [2,3] all have very significant effects upon the output of the thermocell. Both homogeneous [2,3] and heterogeneous [1] electrocatalysis have very significant effects upon the current and therefore overall power output.

The nature of the redox species itself is a multifaceted topic of consideration; ferri/ferrocyanide is one of the most frequently reported thermogalvanic redox couples, but also represents a significant risk to users [4]. Exploration into 'greener' iron redox couples will be introduced [4,5]. Water is a desirable solvent, but also places limitation upon the overall entropy change possible, therefore glymes [6] and ionic liquids [7,8] will also be discussed as potential alternatives.

Finally, the design and accurate testing of the device is a critical step before real-life adoption can be realised. The fundamental aspects required for accurate measurement of thermocells [2,9] and the design aspects relating to in-series and in-parallel combinations [1,4] will be discussed, and finally the concept of 'genuine' or 'total' efficiency [10] of the thermocell at converting a heat source (such as waste heat) into electricity will be discussed.

References

- [1] M. Al Maimani, J.J. Black, L. Aldous. *Electrochemistry Communications* 72 (2016) 181.
- [2] M.A. Buckingham, S. Hammoud, H. Li, C.J. Beale, J.T. Sengel, L. Aldous. *Sustainable Energy and Fuels* 4 (2020) 3388.
- [3] M.A. Buckingham, K. Laws, H. Li, Y. Kuang, L. Aldous. *Cell Reports Physical Sciences* 2 (2021) 100510.
- [4] M.A. Buckingham, K. Laws, J.T. Sengel, L. Aldous. *Green Chemistry* 22 (2020) 6062.
- [5] M.A. Buckingham, K. Laws, E. Cross, A.J. Surman, L. Aldous. *Green Chemistry* 23 (2021) 8901.
- [6] J.J. Black, T. Murphy, R. Atkin, A. Dolan, L. Aldous, *Physical Chemistry Chemical Physics* 18 (2016) 20768.
- [7] E.H.B Anari, M. Romano, W.X. Teh, J.J. Black, E. Jiang, J. Chen, T.Q. To, J. Panchompoo, L. Aldous. *Chemical Communications* 52 (2016) 745.
- [8] L. Aldous, J.J. Black, M.C. Elias, B. Gélinas, D. Rochefort. *Physical. Chemistry Chemical Physics* 19 (2017) 24255.
- [9] M.A. Buckingham and L. Aldous. *Journal of Electroanalytical Chemistry* 872 (2020) 114280.
- [10] M.A Trosheva, M.A Buckingham and L. Aldous. *Chemical Science* 13 (2022) 4984.

Proton-coupled electron transfer reaction for smart thermocells

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Recently, thermo-electrochemical cells, thermogalvanic cells, or thermocells have attracted significant attention due to their practical thermoelectric conversion efficiency. In principle, liquid electrolytes are suitable for heat transport and may outperform semiconductor thermoelectric devices. Our group is enthusiastic about developing novel electrolytes, specifically thermo-responsive systems for thermocells. One important criterion is the proton-coupled electron transfer (PCET) phenomenon. The PCET reaction is widely used in catalytic chemistry, enzyme reactions, and photoelectrochemistry, wherein the transfer of a proton from a substrate is accompanied by an electron transfer reaction. From our point of view, PCET can generate the Seebeck coefficient by the large solvation entropy of a proton with a small ionic radius.

In our presentation, we will cover two topics.

(i) Multiple proton transfer for a high Seebeck coefficient of thermocells [1]

A redox pair of $[\text{Ru}(\text{H}_x\text{im})_6]^{2+/3+}$ (Him=imidazole, $x = 0$ or 1) releases three protons in their one-electron redox reactions in thermocells, resulting in a S_e of -3.7 mV K^{-1} , as confirmed by temperature-dependent square wave voltammetry and thermocell measurement. The value of S_e is proportional to the redox reaction entropy (ΔS_{rc}), which increased with the number of dissociating protons by changing the pH of the solution. By searching the multiple-proton-one-electron PCET reaction, we find a vanadium aqua complex that is suitable for the real application, which surpasses the ZT value of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ system. This result demonstrates the utility of the PCET reaction in achieving efficient thermoelectric conversion.

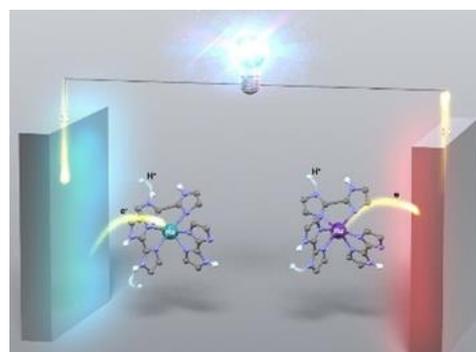


Figure 1. PCET reaction for thermocell.^[1]

(ii) Combination of the pH-changing polymer by phase transition and a PCET molecule [2]

The PCET equilibrium changes its redox potential by pH, and we focused on temperature-responsive pH change. Poly (N-isopropyl) acrylamide (pNIPAM) is known to show hydrophilic-hydrophobic phase transition at ca. $30 \text{ }^\circ\text{C}$ and can change the pH of the solvent by the copolymerization of acrylic acid or amine-functionalized acrylamide. They generate a pH gradient of up to 0.049 and -0.053 pH K^{-1} , respectively, around the phase-transition temperature. The pH gradient triggers the proton-coupled electron transfer (PCET) reactions of quinhydrone on the electrodes, resulting in the highly efficient thermoelectric conversion with a Seebeck coefficient (S_e) of -6.7 and $+6.1 \text{ mV K}^{-1}$. Thermocells driven by the phase transition of hydrogels provide a nontoxic, flexible, and inexpensive charger that harvests carbon-free energy from abundant energy sources such as solar, body, and waste heat.

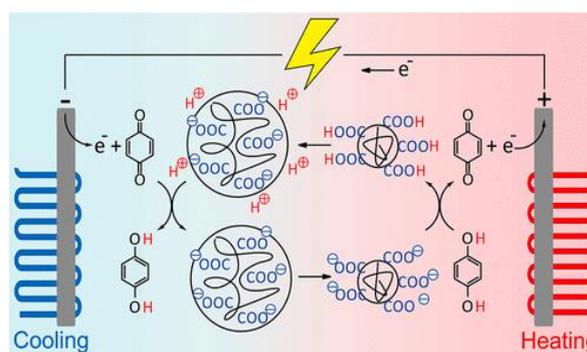


Figure 2. PCET reaction with pH-changing polymer^[2]

References

- [1] T. Kobayashi, T. Yamada, N. Kimizuka, *Chem. Eur. J.* 27 (2020), 4287.
- [2] B. Guo, Y. Hoshino, F. Gao, K. Hayashi, Y. Miura, N. Kimizuka, T. Yamada, *J. Am. Chem. Soc.* 142 (2020), 17318.

Investigation of the performance of a nanostructured and porous Sb-doped tin oxide electrode in a thermo-electrochemical cell

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Low-grade heat (<150 °C) is an abundant and ubiquitous energy available in our surroundings. In the last 10 years thermo-electrochemical cells (also known as thermocells or thermogalvanic cells) have gained attention as a valid option to harvest this vast amount source of energy and find potential applications for the internet-of-things [1].

In order to obtain large power outputs, many thermocells use porous electrodes, such as carbon nanotubes, bucky paper, etc. [2]. Here, we have fabricated different thermocells with nanostructured and porous antimony-doped tin oxide (Sb:SnO₂) electrodes in contact with a 0.4 M aqueous ferro/ferricyanide solution. Their performance was evaluated and compared with the standard Pt electrodes. The same Carnot-related efficiency value (0.040%) was observed for the oxide and the Pt electrodes. To our knowledge, this is the first time that a porous oxide is employed in these systems. Our results offer a suitable alternative to replace the expensive Pt electrodes, which is also advantageous due to the higher chemical stability of oxide-based electrodes.

References

- [1] H. Zhou, H. Inoue, M. Ujita and Tepppei Yamada. *Angew. Chem. Int. Ed.* 62 (2023) 1-18.
- [2] W. Li, J. Ma, J. Qiu and S. Wang. *Mater. Today Energy* 27 (2022) 101032

Thermoelectrochemical redox systems for low temperature grade energy harvesting

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Thermoelectric (TE) devices and thermoelectro-galvanic (TEG) cells harvest energy by converting waste-heat (dissipative form of energy) into electrical energy (precious form with conveyable features). The combination of features like processability, flexibility, lightweight, nontoxicity, low thermal conductivity and high chemical stability in organic electric conductors make them novel palatable materials for thermal energy conversion.

With these premises, the research activity intends to focus on the employment of different novel TE/TEG active materials and devices configurations based on the opportune combination of organic materials (polymer, oligomer or single molecule) with switchable electrical conductivity. The capability of modulating the electrical conductivity in organic materials (over several orders of magnitude) through chemical, electrochemical and chemical-physical processes, will bring about a relevant modulation in the corresponding TE/TEG properties. The research proposed considers design of devices based on organic electrolytes composed of self-standing dissolving matrices with ionophore/ionogenic species to give a non-fluid ionic conductor. The new electronic and ionic organic conductors will be interfaced to realize TE/TEG devices of novel conception benefiting from the versatility of the synthetic chemistry/electrochemistry of the organic conductors to prepare, which will have both electronic and ionic carriers. This leads to the hybridization of the thermal transport properties, particularly useful to develop TE/TEG devices with unique thermal/charge separation properties.

The available versions of TEG mostly consider metallic/graphite electrodes and aqueous/gel-like solutions [1] with electrolytes containing the redox couples $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$, I^-/I_3^- , $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Sn}^{4+}/\text{Sn}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ [2]. TEG systems could reach S values as high as 2.5 mV/K [3]. For this latter type of TE device few examples of organic conductors (either with electron, ion or mixed transport) have been reported [4] for application involving the transformation of low levels of heat waste.

In TEG systems the Seebeck coefficient seems to be related to the entropy of the process, so we present our results adopting for the TEG device redox couples with a large rearrangement energy, which even if slow, should give rise to a major entropy change and thus make it more efficient. Solvation effects are also important so solvent tuning should be tried secondly. Among the quite slow pairs, we focus the study on the cobalt mediators, like the $\text{Co}(\text{II})/(\text{III})$, that present a process with a large rearrangement energy for the spin flip from $\text{Co}(\text{II})$ to $\text{Co}(\text{III})$.

References

- [1] ACS Appl. Energy Mater. 2022, 5, 2130; Nano Energy 2019, 57, 473; Nano Energy 2022, 93, 106795
- [2] Adv. Funct. Mater. 2012, 22, 477; Chem. Commun. 2011, 47, 6260; J. Electrochem. Soc. 1995, 142, 3985; Faraday Discuss. 2016, 190, 205
- [3] J. Electron. Mater. 2016, 45, 3383
- [4] J. Mater. Chem. A, 2022, Advance Article (doi: 10.1039/D2TA00025C); ISCIENCE 2022, 24, 103466

Thermoelectricity in nanofluids: Is there a future?

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Thermoelectrochemical cells with high Seebeck coefficients are paving new research and application directions in the field of thermoelectricity. Despite their resource efficiency (the use of abundant and non-critical elements), facile and low-cost synthesis methods and high shape-versatility, their low electrical (and ionic) conductivity and the limited range of operational temperature reduces their technological competitiveness compared to the solid-state counterpart, *i.e.*, inorganic semiconductors. To illustrate, the state-of-the-art Bi₂Te₃-alloys have the ZT (figure of merit) values exceeding 2 at operating temperatures above ~400°C [1], while the corresponding values for water-based thermoelectrochemical cells are in the range of 10^{-3~2} operating at temperatures below 100°C [2]. As a possible source of renewable electricity, therefore, one should seek for low-power/low-temperature and/or large-size applications for these liquid thermoelectric (TE) materials.

In this presentation, I will first describe recent findings on various TE phenomena in a class of liquids called ‘nanofluids,’ where the thermoelectro-diffusion of charged nanoparticles and the associated interface phenomena are coupled with the thermoelectrochemical (thermogalvanic) effect. Then an example application opportunity of such nanofluids, namely, hybrid-solar thermal collectors (STC) will be presented. In an STC, a large surface area (~m² and larger) is exposed to sunlight for generating heat for domestic hot-water supply. Conventional low-to-mid temperature STCs consist of a dark surface devoted to absorbing the sunlight and to exchanging heat with a thermal fluid. These systems are known to suffer from efficiency limitations due to the thermal resistance at the absorber-fluid interface. A substantial improvement can be expected by the nanofluid-based direct-absorption solar collector (DASC) scheme, with nanofluids working both as a volumetric light absorber and a heat exchanger [3]. Our recent tandem experimental investigations on the thermoelectric and the optical properties of stable aqueous nanofluids show simultaneous enhancement of radiation absorption and thermoelectric power-output with only a very small volume fraction of nanoparticles [4].

Lastly, if time permits, I will also present a new COST-Action “EU-MACE” (European Materials Acceleration Center for Energy). EU-MACE aims to create a network of MAPs (Materials Acceleration Platforms) across Europe, which may provide new research opportunities to the thermoelectrochemical research community.

References

- [1] See for example, X. L. Shi, et al., Chem. Rev. 120, 7399–7515 (2020).
- [2] Estimated values from, L. Zhang, et al., Adv. Mater. 29, 1605652 (2017); T. Salez, PhD thesis, Ecole Normale Supérieure, France (2017).
- [3] Z. Liu, et al., Therm. Sci. Eng. Prog. 8, 130 (2018).
- [4] E. Sani, et al., Nanomaterials, 11 1031 (2021).

Study of thermocells using ferricyanide/ferrocyanide and their application to self-powered sensors

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Thermocells, also known as thermogalvanic or thermos-electrochemical cells, are devices that convert heat directly into electrical energy using the principles of electrochemistry. Thermocells consist of two electrodes immersed in an electrolyte solution. When there is a temperature difference between the two electrodes, it creates a potential difference across the electrodes, given by the Nernst equation:

$$E = E_T^0 - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

Where: E is the electrode potential, T is the temperature, E_T^0 is the standard electrode potential at T , R is the ideal gas constant, n is the number of electrons transferred in the redox reaction, F is Faraday's constant, $[Red]$ the concentrations of the reductant and $[Ox]$ the concentrations of the oxidant. The open circuit voltage of the thermocells should be determined by the temperature dependence of the standard electrode potentials and the concentration terms.

In this presentation, we first compare thermocells using ferricyanide/ferrocyanide with and without guanidinium (Gdm^+) under different loading conditions.^[1] Compared with ferricyanide/ferrocyanide-based devices, the device with guanidinium-added electrolytes shows higher power and energy densities. We observed that the enhanced performance is not due to the ionic Seebeck effect of guanidinium but because of the configuration entropy change (the concentration terms) resulting from the selective binding of Gdm^+ to $Fe(CN)_6^{4-}$.^[2,3] However, the device with guanidinium-added electrolyte exhibits high anisotropy and does not show steady-state operation. We believed that could be attributed to the difficult diffusion of $Fe(CN)_6^{3-}$ into the crystal layer of $(Gdm^+)_n[Fe(CN)_6^{4-}]$ at the hot electrode and the difficult precipitation of $(Gdm^+)_n[Fe(CN)_6^{4-}]$ formed at the cold side upon the binding of the reduced $Fe(CN)_6^{4-}$ with Gdm^+ .

Next, we will examine the thermocells using the agar-gelled electrolyte.^[4] In the agar-gelled electrolyte, the ions are homogeneously distributed in the polymer matrix because it forms from a solution at high temperatures. A high value for the Seebeck coefficient (S_e) was observed whether the heat source was placed in correspondence with the bottom electrode or the top electrode. The large S_e and isotropic properties could constitute a major advancement in the utilization of low-temperature heat, such as body heat and solar thermal heat. We believe that the high S_e value should also be attributed to the configuration entropy change.

Finally, we also compare the thermocells in H_2O and D_2O . As a result, the thermocells in D_2O always show a higher S_e value which should be related to the difference in temperature-dependence change in standard electrode potentials. An attempt is made to understand the contribution of the standard reaction entropy and the concentration term.^[5,6] We will show a demonstration of a self-powered sensor that uses body temperature to wirelessly transfer humidity, temperature, and barometric pressure data.

References

- [1] B. Yu et al. *Science*, 370 (2020), 342.
- [2] V. Nandal, Q. Wei, and K. Seki. *Phys. Chem. Chem. Phys.*, 23 (2021), 14803.
- [3] L. Jiang et al. *ACS Appl. Mater. Interfaces*, 14 (2022), 22921.
- [4] L. Jiang et al. *Global Challenges*, 2023, 2200207.
- [5] B. Huang et al., *Phys. Chem. Chem. Phys.*, 20 (2018), 15680.
- [6] M. Buckingham et al. *Sustainable Energy Fuels*, 4 (2020), 3388.

Thermogalvanic energy conversion improvement in ionic liquids: redox solvation and coordination chemistry

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Thermogalvanic cells (or thermocells) utilize a temperature difference across the electrodes immersed in an electrolyte solution to drive the electrochemical (redox) reactions that generate an electric potential and current. Solid thermoelectric devices, on the other hand, function as thermodynamic engine to directly convert heat into electricity or vice versa. For both systems, the first indicator of the thermal-to-electric energy conversion capacity is the materials' Seebeck coefficient; i.e., the ratio between the applied thermal energy (ΔT) and the extracted electric energy (ΔV).

Among different types of thermocells, those made with room temperature ionic liquids not only have high Seebeck coefficient but also present technologically and environmentally desirable properties: e.g., a wide electrochemical range of stability, thermal stability (>200 °C, low toxicity and volatility, making this class of devices greener and more sustainable. It has been shown that the primary factor affecting the reaction potential in ionic liquids resides in the close vicinity of the redox pair near the electrode surfaces, more so than the liquid medium itself. In the present study we take a closer look at the effect of solvated water molecules in on a bare ion redox pair of europium ($\text{Eu}^{2+/3+}$) and a strongly complexed cobalt, $[\text{Co}(2,2'\text{-bipyridine})_3]^{2+/3+}$ in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI) in the range of H_2O content between <500 and 16000 ppm. It is found that depending on the redox species, water molecules can coordinate with the metal ions, leading to marked changes in their structural and electrochemical behavior of the complexes. In the long term, exploring how to utilise the solvation and coordination chemistry of redox species will help advance our understanding of the fundamentals of the thermogalvanic effect in complex media, and simultaneously, enable the fine-tuning of the thermocell efficiency toward their industrial exploitations.

Soft thermoelectric materials based on hydrogels

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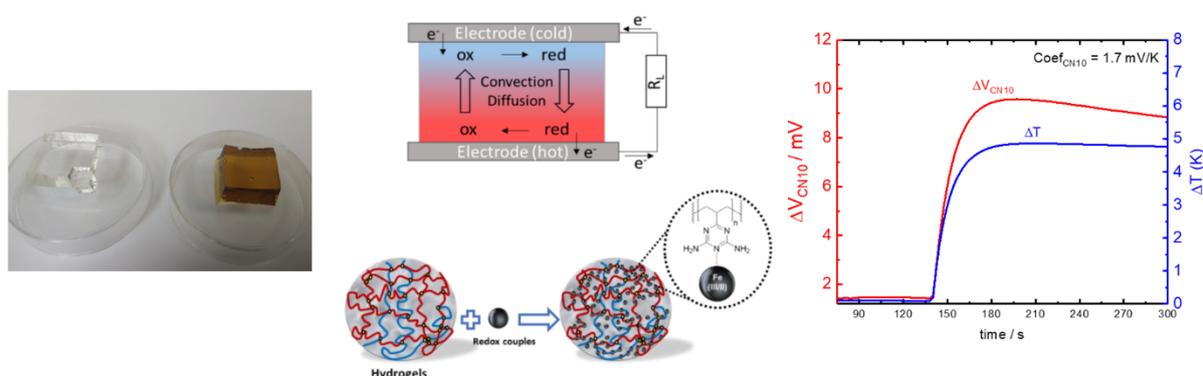
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Organic compounds are interesting for the thermoelectric conversion due to their abundance and sustainability, resulting in a cheap and versatile approach towards energy harvesting. In addition, they offer the possibility to design soft and flexible devices and also the ability to profit from non-conventional thermoelectrical effects such as the thermogalvanic effect [1], which we develop in this work. Through this effect, a temperature difference in an electrolyte produces the gradient of a redox couple which reacts at electrodes producing a charge difference and current.

Here focus is on electrolytes based on gels which offer advantages over conventional liquids related to their better stability and safety [2]. We employ a *Digital Light Processing* printer, settled to print hydrogels, which allows designing specific shapes and sizes offering a large versatility. We have prepared hydrogels with different functional groups to explore the ability to anchor different redox couples: $\text{Fe}^{3+/2+}$ and $\text{Fe}(\text{CN})_6^{4-/3-}$ among others. The influence of the couple concentration, the swelling (water content) and the type electrode over the thermogalvanic behavior and the output power has been analyzed.



References

- [1] C-G. Han et al., *Science* 368, 1091 (2020).
- [2] Y. Zhang et al., *Nature Communications* 12, 5269 (2021).
- [3] M. Massetti et al., *Chemical Reviews* 121, 12465 (2021).

Increasing the entropy change in thermocells by intermolecular forces

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Thermocells produce electric power out of temperature gradient between a pair of electrodes immersed in a liquid electrolyte. Seebeck coefficient (S_e) of thermocells is proportional to the entropy change of the redox reaction taking place at the electrode surface (ΔS_{redox}):

$$S_e = \frac{\partial E}{\partial T} = \frac{\Delta S_{\text{redox}}}{nF}$$

To increase the S_e , our group have been focused on using intermolecular forces between the redox species and the additives or the polymer chains to increase the ΔS_{redox} . In 2016, we demonstrated the first example of using host-guest interaction in thermocell to increase the S_e . α -cyclodextrin (α -CD) in aqueous iodide/triiodide (I^-/I_3^-) electrolyte selectively captures I_3^- at the cold side and release it at the hot side to create the concentration gradient of I_3^- (**Figure 1a**). [1] More recently, we reported the entropy change induced by the host-guest interaction between I_3^- and the CDs with various cavity sizes and degree of methylation shows the linear relationship with the increment of S_e induced by the addition of the CD (Figure 1b). This result shows the host molecules causing larger entropy changes is advantageous for inducing a greater increment of S_e in thermocells.

In 2020, we reported that addition of nanoparticles of thermo-responsive polymer (PNIAPM) in aqueous quinhydrone thermocell creates the pH gradient between the hot and cold electrodes, and the S_e values were increased up to -6.7 or $+6.1$ mV K^{-1} , depending on the acidity or basicity of the polymers. [3] Recently, we found out that the entropy change induced by the coil-globule phase transition of a redox-active polymer (PNV) is indeed correlated with the increment of S_e observed above the phase transition temperature (Figure 1c, d). Currently, we are working on an amphiphilic redox-active polymer, which self-assembles into thermo-responsive micelles and shows a large S_e value. In this presentation, we introduce a brief overview of the studies carried out in our group and finally provide future perspectives for designing the intermolecular interactions in thermocells.

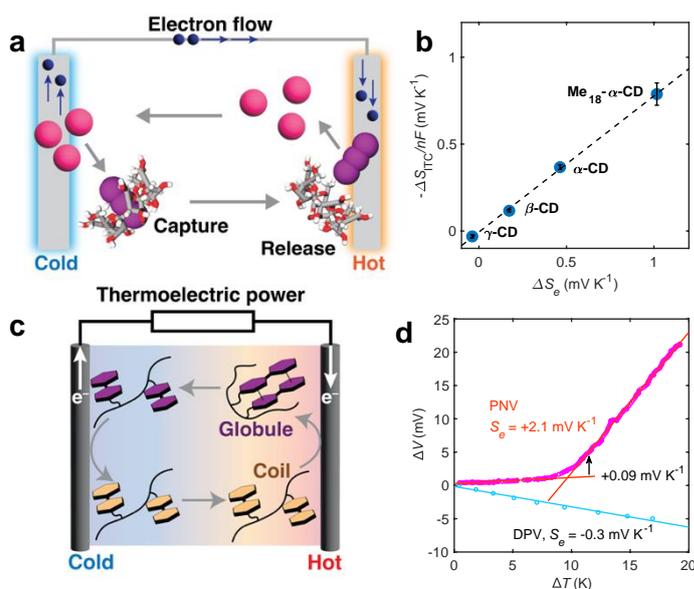


Figure 1.

- Schematic showing α -CD capturing and releasing I_3^- to increase the S_e value
- Linear relationship between the increment of S_e values induced by the addition of various CDs and the entropy change measured by isothermal titration calorimetry (ITC)
- Schematic showing the coil-globule phase transition of the redox polymer (PNV) to increase the S_e value
- Drastic increase of open-circuit voltage at the phase transition temperature of PNV ($\Delta T \sim 10$ K)

References

- [3] H. Zhou, T. Yamada, N. Kimuzuka, *J. Am. Chem. Soc.* 138 (2016) 10502.
- [4] H. Zhou, H. Inoue, M. Ujita, T. Yamada, *Angew. Chem. Int. Ed.* 62 (2023) e202213449.
- [5] B. Guo, Y. Hoshino, F. Gao, K. Hayashi, Y. Miura, N. Kimizuka, T. Yamada, *J. Am. Chem. Soc.* 142 (2020) 17318.

Oral contributions

Topic:

Ionic thermoelectric supercapacitors

Ionic thermoelectric supercapacitors

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Redox-free electrolytes have been poorly explored in thermoelectric applications due to a lack of strategies to harvest the energy from the Soret effect. In recent years, several reports displayed high values of ionic Seebeck coefficients (up to 30 mV/K) resulting from the concentration gradients of ionic charged species in electrolytes [1]. The remarkably strong ionic Soret effect in polymeric electrolytes has been advantageously used to charge electric double layers at large area electrodes. The resulting ionic thermoelectric supercapacitor (ITESC) is charged under a temperature gradient [2]. After the temperature gradient is removed, the stored electrical energy can be delivered to an external circuit. This new means to harvest energy is particularly suitable for intermittent heat sources.

While traditional electronic thermoelectric materials are classified using a figure of merit ZT_e , it has been unclear how to best evaluate the performance of ionic thermoelectric materials. Indeed, these systems cannot be directly used in a traditional thermoelectric generator because they are based on ions that cannot pass the interface between the thermoelectric material and external metal electrodes. The charging efficiency of the ITESC can be quantitatively related to the figure of merit $ZT_i = \sigma_i S_i^2 T / \lambda$, where σ_i is the ionic conductivity, S_i is the ionic Seebeck coefficient and λ the thermal conductivity. This means that the performance of ionic thermoelectric materials can also be compared and predicted based on the ZT_i . However, it is important to note that ZT_i cannot be compared directly to ZT_e and more will be discussed about that crucial comparison [3].

We have lately identified several phenomena that produce an extra voltage, which are typically neglected when measuring the ionic Seebeck coefficient. Those phenomena might thus lead to erroneous and overestimated values of the ionic Seebeck coefficient. More interestingly, the same phenomena can be exploited for energy harvesting in the ITSECs. For instance, the presence of water evaporation and condensation at the surface of the electrolyte submitted to a temperature gradient lead to a hydrovoltaic voltage [4]. It has also been found that interfacial phenomena (chemisorption, Donnan potential) between the electrode and the electrolyte can lead to additional interfacial potential drop that is temperature dependent; as a result, there is an additional interfacial contribution to the measured thermo-induced voltage [5,6].

Besides considering various ionic thermoelectric materials, the design of ITSECs has been developed further by changing the nature of the electrode. First considering microporous carbon electrodes, then moving towards all-polymeric ITSECs using organic conducting polymer electrodes [6]. Recently, even stretchable ITSEC have been demonstrated with both stretchable electrodes and stretchable electrolyte [7].

References

- [1] Dan Zhao, Alois Würger, Xavier Crispin, *Journal of Energy Chemistry* 61 (2021) 88.
- [2] D. Zhao, H. Wang, Z. U. Khan, J. C. Chen, R. Gabrielsson, M. P. Jonsson, M. Berggren, X. Crispin, *Energy Environ. Sci.*, 9, (2016) 1450.
- [3] H. Wang, D. Zhao, Z. U. Khan, S. Puzinas, M. P. Jonsson, M. Berggren, X. Crispin, *Adv. Electron. Mater.* 3 (2017) 1700013.
- [4] D. Zhao, A. Sultana, J. Edberg, M. Shiran Chaharsoughi, M. Elmahmoudy, U. Ail, K. Tybrandt, X. Crispin, *J. Mater. Chem. C*, 10 (2022) 2732.
- [5] S. Mardi, D. Zhao, N. Kim, I. Petsagkourakis, K. Tybrandt, A. Reale, X. Crispin, *Adv. Electron. Mater.* 7 (2021) 2100506.
- [6] S. Mardi, D. Zhao, K. Tybrandt, A. Reale, X. Crispin, *Adv. Mater. Interfaces* 9 (2022) 2201058
- [7] T. H. Park, X. Crispin et al. *Nano Energy* 114 (2023) 108643.

Gelatin-based ionic thermoelectric gel for energy harvesting

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Harvesting heat from the environment into electricity has the potential to power Internet-of-things (IoT) sensors, freeing them from cables or batteries and thus making them especially useful for wearable devices. In this work, we demonstrate a giant positive thermopower up to 24 mV/K in a flexible, quasi-solid-state, ionic thermoelectric material using synergistic thermodiffusion and thermogalvanic effects. The ionic thermoelectric material is a gelatin matrix modulated with ion providers (KCl, NaCl, and KNO₃) for thermodiffusion effect and a redox couple [Fe(CN)₆⁴⁻/Fe(CN)₆³⁻] for thermogalvanic effect. Furthermore, the strategies of three-dimensional electrodes and working temperature enlarging were used to boost the energy output, realizing a record-high power density of 9.6 mW m⁻² K⁻² and a 2 h energy density (E_{2h}) of 198 J m⁻². Some new progress in ionic thermoelectric figure of merit will also be discussed.

References

- [1] C. H. Han, X. Qian, Q.K. Li, B. Deng, Y.B. Zhu, Z. J. Han, W. Q. Zhang, W. C. Wang, S. P. Feng, G. Chen, W.S. Liu. *Science* 368 (2020) 1091-1098.
- [2] Y.C. Li, Q. K. Li, X.B. Zhang, B. Deng, C. G. Han, W. S. Liu. *Adv. Energy Mater.* (2022)210366
- [3] Y.C. Li, Q. K. Li, X. B. Zhang, J.J. Zhang, S. H. Wang, L.Q. Lai, K. Zhu, W. S. Liu. *Energy Environ. Sci.* 15(2022)5379-5390.

Lignin-derived ionic thermoelectric hydrogels for low-grade thermal energy harvesting

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Sustainable materials have become an increasingly important area of research due to the increased need for environmentally friendly alternatives to traditional materials. Lignin, a paper and pulp industry waste product, has attracted significant attention in recent years as a promising sustainable material for high-end energy applications [1]. In this study, we synthesised lignin-based hydrogel to be used as ionic thermoelectric materials for low-grade thermal energy harvesting [2]. Ionic thermoelectric performance was evaluated by examining the effects of lignin, crosslinker, and electrolyte concentration on the Seebeck coefficient, ionic conductivity, and power factor. Our findings revealed that the increase of lignin content in the hydrogel matrix improved the ionic thermoelectric performance. Crosslinker and electrolyte concentrations also significantly influenced the thermoelectric properties of the material. The optimized lignin-derived hydrogel exhibits superior ionic conductivity (225.22 mS/cm), a high Seebeck coefficient of 6.723 mV/K, and an exceptional power factor of 1029.74 $\mu\text{W}/\text{mK}^2$ under the application of an axial temperature gradient. This study will open many areas of research in the field of low-grade thermal energy harvesting and pave the way for the development of sustainable, environmentally friendly, and cost-effective energy harvesting devices.

References

- [1] M. Culebras, H. Geaney, A. Beaucamp, P. Upadhyaya, E. Dalton, K.M. Ryan, M.N. Collins, *ChemSusChem*, 12 (2019) 4516-4521.
- [2] Y. He, Q. Zhang, H. Cheng, Y. Liu, Y. Shu, Y. Geng, Y. Zheng, B. Qin, Y. Zhou, S. Chen, *The Journal of Physical Chemistry Letters*, 13 (2022) 4621-4627.

Nanowood: Fully renewable, biodegradable, environmentally friendly, natural material for the next generation thermoelectrics

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The rapid increase in the temperature of the Earth's atmosphere, caused by man-made factors, is one of the most serious threats of our time. The most important measure to mitigate this threat is to reduce carbon emissions through an energy transition, i.e. switching from fossil fuel energy sources to renewable energy sources that produce very limited, if not zero, carbon emissions. One such source of clean energy is thermoelectric generators that can directly convert thermal energy into electrical energy. In this presentation, we discuss the production process of a new ionic thermoelectric material - nanowood. We describe the technology of nanowood production, as well as its practical use in ionic thermoelectric supercapacitors. We show that, due to the nanoconfinement effect, nanowood-based supercapacitors allow generating thermoelectric voltages that are an order of magnitude higher than those for devices based on bulk electrolytes.

Oral contributions

Topic:

Other thermo-electrochemical devices

Thermovoltage generation with thermally activated electrolytes

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A number of thermoelectric materials that show a very pronounced thermoelectric response have been reported in the literature. The Seebeck coefficient, a measure of the thermovoltage generated per temperature difference applied across a layer of material, is often higher for electrolyte-filled nano-confinements than for solid-state thermoelectric devices. Recently, it was reported that room-temperature ionic liquids (RTILs) and highly concentrated aqueous electrolytes, despite having large ion concentrations, yield electric double layers with a thickness of some nanometers [1]. This can be explained by the fact that the charge carriers in these electrolytes are not the elementary ionic constituents but are pseudoparticles, i.e. clusters of many ions which can partially dissociate in a thermally activated process. The number density of the effective charge carriers in such thermally activated electrolytes (TAEs) is, therefore, a function of temperature and is usually described by an Arrhenius equation. We study the thermovoltage generation in such TAEs using a theoretical framework based on the coupled Poisson-Nernst-Planck and heat transport equations. The results indicate that a TAE yields a significantly higher Seebeck coefficient than a dilute electrolyte. This can be explained by the charge carrier concentration gradients that form due to the thermally activated charge carrier formation. The study reveals that confined TAEs bear a significant potential for thermoelectric energy conversion.

Reference

- [1] Gebbie, M. A., Dobbs, H. A., Valtiner, M. Israelachvili, J. N. Long-range electrostatic screening in ionic liquids, PNAS, 2015, 112, 7432–7437.

Performance parameters for ranking the techniques for low-temperature heat exploitation

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Several innovative techniques have been recently proposed for the exploitation of low-temperature heat sources, around or below 100°C. Some are aimed at "energy scavenging", e.g. for powering portable electronic devices or devices not connected to the power grid. Many others are seen as mean for providing clean and renewable energy and mitigating the global problem of CO₂ emission. For this second class of applications, suitable performance parameters must be developed in order to provide an effective ranking.

We performed a thermodynamic analysis of the various techniques [1,2], highlighting the physical limitations constituting the bottlenecks for the practical implementation. This analysis led to the development of suitable performance parameters. The most obvious are the power density and the energy efficiency. In order to increase the latter, many studies suggest the use of additional heat circuits, including heat exchangers. The heat exchangers are often considered as ideal; under this erroneous assumption, almost all the techniques reach a similar energy efficiency. With a more realistic modelling of the heat exchangers, in many techniques, cumbersome heat exchangers would be needed, making them impractical. A suitable ranking thus requires to take into account the size of heat exchangers needed to produce a unit power.

In order to better connect the performances to the physical limitations of the techniques, we also developed an intrinsic characterization, based on two parameters: the "intrinsic efficiency" and the "intrinsic temperature difference". These two parameters do not depend on the use of external heat exchangers and enable an overall ranking of the various techniques.

References

- [1] D. Brogioli, F. La Mantia. *Energy Environ. Sci.* 14 (2021) 1057.
- [2] D. Brogioli, F. La Mantia. *Adv. Energy Mater.* 30 (2022) 2103842.

Thermoelectric Characterization of Electrodeposited Materials and its Application in Micro Thermoelectric Devices

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Micro-thermoelectric devices offer immense potential for various applications in the biomedical field, powering Internet of Things (IoT) devices, and thermal management. The successful optimization of the thermoelectric figure of merit, denoted as zT , plays a crucial role in enabling the practical implementation of these devices. However, characterizing the thermoelectric properties of films grown through electrochemical deposition, a common technique for fabricating micro thermoelectric (TE) devices, remains a significant challenge. In such cases, TE materials are deposited onto an electrically conductive seed layer, resulting in in-plane short-circuiting, which hinders the unambiguous determination of transport coefficients.

In this study, we present novel characterization techniques to accurately assess the thermoelectric properties and contact resistance of electrochemically deposited materials, specifically designed for micro TE devices. To overcome the limitations imposed by the electrically conductive seed layer and substrate, we introduce a characterization platform that enables full in-plane zT characterization of electrochemically deposited TE materials [1]. This platform utilizes a suspended TE material within a transport device, fabricated through a combination of photolithography and etching processes. By eliminating the influence of the seed layer and substrate, this comprehensive in-plane zT characterization represents a significant milestone for optimizing materials under realistic conditions in micro TE devices. Additionally, we introduce a Cox-Strack setup, which allows us to determine the contact resistance associated with the electrochemically deposited materials. Furthermore, we discuss the TE characterization of these materials and their potential applications in micro TE devices [2]. Overall, our research contributes to the advancement of characterization techniques, providing valuable insights for optimizing the performance of electrochemically deposited materials in the realm of micro thermoelectric devices.

[1] Barati et al., *Advanced Electronic Materials* **6**, 1901288 (2020).

[2] Dutt et al., *Advanced Electronic Materials*, 2101042 (2022).

Height Optimized Micro-Thermoelectric Devices

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Electrochemical deposition is an excellent choice for the fabrication of Micro thermoelectric devices that can be used for hot spot cooling and energy-autonomous sensor applications in combination with fabrication methods that are fully compatible with on-chip integration.

Electrochemical deposition offers advantages over other techniques due to its compatibility with lithography, high deposition rates, tunable material composition, cost effectiveness and large scalability. To achieve maximum device performance, the geometry of the device must be optimized to match the electrical and thermal properties of the thermoelectric materials to maximize the ZT of the device. This is usually done by adjusting the cross-sectional areas which leads to a limitation of the maximum packing density. Here, we present a new design strategy for the fabrication of uTEDs in which we optimize the heights, allowing higher packing densities, thereby increasing the cooling power density and output power, and also reducing the amount of thermoelectric materials needed required, which are often toxic and expensive. Electrochemical deposition gives us the flexibility to vary the geometry of the device according to our interests.

To fabrication of the micro thermoelectric devices, we use photolithography combined with the electrochemical deposition of $\text{Bi}_2(\text{Te}_x\text{Se}_{1-x})_3$ and Te as n-type and p-type materials, respectively [1,2]. We have introduced N_2 bubbling into the electrolyte prior to the deposition in order to reduce the amount of oxygen in the resulting deposition, which in turn reduces the contact resistance, resulting in higher ΔT and cooling power density. We have also implemented geometry optimization in to the fabrication process to increase the ZT of the device, which is critical for better device performance. The maximum cooling of area optimized and height optimized uTECs is 10.8 K and 10.5 K at room temperature, respectively. Finite element simulations show that cooling power densities of hundreds of watts per square centimeter can be achieved for both. The height optimized uTECs shows a maximum cooling of 21 K at an ambient temperature of 343 K and uses 75% less Te than area optimized devices [2]. As a generator, the micro thermoelectric modules exhibit high open-circuit voltages and power densities in the range of a few milliwatts per square centimeter even at small temperature differences. Our results demonstrate the excellent suitability of micro thermoelectric modules for hot-spot cooling applications to increase integration density in circuits and energy-autonomous sensors for the Internet of Things.

References

- [1] A, Dutt et al Adv. Electron. Mater. **2022**, 2101042
- [2] Li, Guodong, et al. Nature Electronics 1.10 (2018): 555.

Large increase in the electrical conductivity with small change in the Seebeck coefficient for a nanostructured and porous oxide in contact with a solid electrolyte

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The energy conversion efficiency in a thermoelectric material relies on the dimensionless figure of merit $zT = S^2 \sigma T / \kappa$, being S the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature. The product $S^2 \sigma$ is known as the power factor (PF). Recently, large PF enhancements have been shown in a novel hybrid solid-liquid thermoelectric system, consisting of a porous nanostructured solid material (Sb-doped SnO₂) in contact with diverse liquid electrolytes [1].

In this contribution, we have investigated the nanostructured Sb:SnO₂ film in contact with polyelectrolytes based on the poly-diallyl dimethylammonium cation (PDADMA). From all the electrolytes tested, the poly-diallyl dimethylammonium chloride (PDADMAC) was found to provide more than 2 times improvement in the power factor. This large improvement was due to a $\approx 60\%$ decrease in the electrical resistance of the device accompanied by a slight reduction of less than 10% in the absolute value of the Seebeck coefficient. Impedance spectroscopy analysis was carried out to understand the role of the polyelectrolyte in the device performance. The significant PF improvement opens up the possibility to use polyelectrolytes to fabricate all-solid-state hybrid solid-electrolyte devices able to improve the thermoelectric PF.

References

- [1] L. Márquez-García et al., ACS Applied Energy Materials 1, 254 (2018).

Poster contributions

Printed p-n type Thermogalvanic Modules for Energy Conversion

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In front of major climate and energy crisis, there is an urge to find solutions to optimize industries in terms of sustainability, production, maintenance. One strategy is to monitor industries with sensors coupled to the internet and analyze data with artificial intelligence. But to wire hundreds of sensors becomes a nightmare, hence low-cost wireless solutions would require a low-cost energy harvesting unit to power the sensors and to send the signals. Various low-power energy harvesters are scrutinized with the goal of charging a supercapacitor and discharge it to get enough power for communication. Piezoelectric, triboelectrics, photovoltaics and thermoelectrics are the classes of energy harvesting devices typically considered.

Thermogalvanic cells (TGCs) are heat-to-electricity conversion devices that have been little investigated in that context. The TGC is, however, a potentially interesting solution because of the low cost of its manufacturing scheme, such as using printing technologies. The TGC generates constant power under constant temperature gradient, utilizes environmentally friendly materials, and presents a high Seebeck coefficient (S_e). TGCs consist of two identical electrodes in contact with a redox electrolyte containing a reversible redox couple. When applying a temperature difference (ΔT) between the two electrodes, the generated thermovoltage is proportional to the difference in entropy between the two redox states of the redox couple ($\Delta V/\Delta T = \Delta S_{rc}/nF$). [1-4] With a constant ΔT , the transport of the redox molecules through migration, diffusion and convection enables continuously power generation to the external circuit. Typically, the S_e values for classical redox active pairs in aqueous solutions are in the range of 1-2 mV/K. which is too low for practical applications. Building thermogalvanic modules (TGMs) that connect multiple TGCs in series can efficiently multiply the output voltages. However, the aqueous electrolytes of low viscosity in TGCs are limiting the scalability and processability of the TGMs in easy and straightforward manufacturing, such as screen printing or stencil printing. Moreover, modifications in the electrolyte are also demanded to reduce the evaporation of water in long term applications (especially because of the applied ΔT) and leakage.

In the present work, we investigated two types of redox couples of opposite S_e in a single TGC with low-cost and printable AC electrodes. The $[\text{Fe}(\text{CN})_6]^{3-/4-}$ presented a S_e of 1.59 mV/K and a maximum power density of 3.54 mW/m², while the $\text{FeCl}_{2/3}$ had -1.67 mV/K S_e and 1.70 mW/m² maximum power density, showing they are compatible for building double-type electrolyte modules. By increasing the number of legs to two and four, we observed an increase in the S_e to 2.36 mV/K and 3.05 mV/K respectively, but the increase in resistance of the devices hindered the amount of power delivered. Finally, we assembled a printed sixteen legs p-n type device as proof of concept, based on copper foil insulated with a plastic coating as a substrate, silver current collector, and the same AC electrodes. By adding a polymer to the redox electrolytes to increase the viscosity, we avoided their inter-mixing and leakage during printing. This device presented a considerable increase in output voltage for a higher number of legs and S_e reached 5.31 mV/K, but still presented a high internal resistance that hindered the power delivery. Although further investigation and improvement are needed, our strategy of improving electrolytes enables printing of TGMs of sixteen legs. This printing method allows for further scalability and was an important step in building multiple legs modules for energy harvesting.

References

- [1] D. Zhao et al. *Journal of Energy Chemistry*, 61. 2021, 88.
- [2] K. Wijeratne et al. *Journal of Material Chemistry A*, 5. 2017, 19619.
- [3] M. Buckingham et al. *Journal of Electroanalytical Chemistry*, 872. 2020, 114280.
- [4] M. Buckingham et al. *Green Chemistry*, 23. 2021, 8901.

Thermoelectrics based on Fe liquid mixtures

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Thermoelectrochemical cells (or thermocells, TCs) are gaining increasing relevance for the recovery of low grade waste heat. The voltage generated by a single TC determines whether they can be used in real applications. In this work, we investigate different Fe-based liquid aqueous/co-solvent mixtures to convert temperature gradients into electricity by the thermogalvanic effect. The organic solvents of choice will exhibit different donor numbers (DNs). The formation of $[\text{Fe}(\text{L})_6]^{2+/3+}$ complexes will be studied with a variety of techniques, including by Raman spectroscopy and extended X-ray absorption fine structure (EXAFS). Any possible correlation between the solvent DN, the nature of $[\text{Fe}(\text{L})_6]^{2+/3+}$ complexes and the Seebeck coefficient of the TG cell will be discussed.

All-organic thermocell with high Seebeck coefficient achieved by the formation of local solvation cage based on hydrogen bond

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Thermocell is an electrochemical system consisting of two electrodes immersed in an electrolyte containing a redox couple. It has attracted much attention thanks to its high Seebeck coefficient (\sim mV K⁻¹) and low thermal conductivity. The coefficient, S_e , of thermocell is proportional to the entropy change in the redox reaction (ΔS_{rc}) and thus can be improved by solvent reorganization in the redox reaction. In this study, we create an effective approach to enhance the S_e value by tailoring selective local solvation with reduced species (Red). A previous report shows that the *p*-chloranil dianion (CA²⁻, Red) is a significantly strong hydrogen-bond (H-bond) acceptor compared to the *p*-chloranil radical anion (CA⁻, Ox).[1] Upon adding ethanol (EtOH, an H-bond donor), the solvation cage of EtOH is formed around CA²⁻ (Red) and is broken down by the oxidation to CA⁻ (Ox). The formation/breakdown of the solvation cage leads to a large ΔS_{rc} , and we achieved the S_e value of 2.6 mV K⁻¹, the highest for all-organic thermocells.

We measured the S_e value for the acetonitrile electrolyte comprised of CA^{-/2-} (0.5 mM) and TBAPF₆ (100 mM) with various concentrations of EtOH (0, 40, 250, or 1300 mM). The S_e value increases with increasing EtOH concentration from 1.3 mV K⁻¹ (absence of EtOH) to 1.8 ([EtOH] = 40 mM), 2.2 ([EtOH] = 250 mM), and 2.6 mV K⁻¹ ([EtOH] = 1300 mM).

We analyzed the EtOH solvation structure around CA⁻ and CA²⁻ by UV-Vis spectroscopy and theoretical calculation. From the UV-Vis spectra, absorption peaks of CA⁻ show negligible shifts with increasing EtOH concentration, while a peak of CA²⁻ shows a significant blue shift. Time-dependent density functional theory (TD-DFT) calculations reveal that the noticeable blue shift of the CA²⁻ peak is due to the out-of-plane contact of EtOH molecules with the O atoms of CA²⁻. The organized structure of the solvation cage around CA²⁻ should create a significantly low entropy state, causing a great entropy change in the redox reaction to CA⁻.

We evaluated the thermodynamic parameters of EtOH association with CA⁻ and CA²⁻ by square wave voltammetry (SWV) and simulated the ΔS_{rc} value at every EtOH concentration. The SWV measurement shows a significant positive potential shift of CA^{-/2-} with increasing EtOH concentration. The positive shift was fitted with a theoretical model from the Nernst equation, thereby yielding the number of EtOH molecules bound to CA⁻ and CA²⁻ and the binding constants. As the EtOH concentration increases, the number of EtOH molecules bound with CA²⁻ increases up to six, while CA⁻ hardly binds with EtOH molecules. For both CA⁻ and CA²⁻, the association entropy increases with the number of bound EtOH molecules. We then simulated the ΔS_{rc} from the association entropy, and the simulated ΔS_{rc} corresponds with the experimental values. The simulated results reveal that the local solvation cage of multiple EtOH molecules around CA²⁻ is broken down in the redox reaction to CA⁻, which produces a significant entropy gain and increases the ΔS_{rc} value.

In conclusion, we create an effective way to enhance the S_e of thermocells using the selective local solvation of H-bond donor molecules to CA²⁻. The solvation cage should be highly ordered because the multiple EtOH molecules are assembled to the O atom of CA²⁻ via ordered H-bonding. The organized solvation cage is broken down in the redox reaction to CA⁻, which results in a significant ΔS_{rc} (S_e). In addition, this method is a versatile way to improve the S_e value among other benzoquinone redox species, and we believe the possibility to open the field of organic thermocells.

References

[1] B. Uno, N. Okumura, M. Goto, K. Kano. *Journal of Organic Chemistry*, 65. (2000) 1448–1455.

Thermally chargeable supercapacitor based on ionic hydrogels with tunable polarity

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Thermally chargeable supercapacitors (TCSs) have the potential to be used as a future component of waste heat recovery because of their high Seebeck coefficients [1]. Here, we will report that ionic hydrogels consisting of imidazolium chloride salts and poly(vinyl alcohol) show the Seebeck coefficients as high as +10 mV K⁻¹. Their high ionic conductivities (>1 mS cm⁻¹) and low thermal conductivities (~0.2 W m⁻¹ K⁻¹) also offer good potential for usage in heat-to-electricity energy conversion system [1].

Further, we investigated the controlling methodology of the polarity (p- and n-type) of TCS. We found that the p-type polarity of the TCS (constructed with metal electrodes) could be converted into n-type (approximately -1 mV K⁻¹) by using poly(3,3-ethylenedioxythiophene):poly(styrenesulfonyl) (PEDOT:PSS) conducting polymer as electrodes [2]. These observations as well as absorption spectroscopy suggest that the temperature-dependent variation of ion distributions in double layer is one of the contributors of voltage generation from TCS.

Finally, we will demonstrate an example of power supply using TCSs. The potential of TCS could be highlighted by modularizing the TCSs electrically in series and thermally in parallel; the voltage from each leg is effectively added to show the large open-circuit voltage of >1.5 V at the temperature difference of ~40 °C. Upon loading with a LED, the induced voltage could be converted into electric current to power the LED.

References

- [1] D. Zhao, H. Wang, Z. U. Khan, J. C. Chen, R. Gabrielsson, M. P. Jonsson, M. Berggren, X. Crispin. *Energy & Environmental Science* 9 (2016) 1450.
- [2] S. Horike, Q. Wei, K. Kirihara, M. Mukaida, T. Sasaki, Y. Koshiba, T. Fukushima, K. Ishida. *ACS Applied Materials & Interfaces* 12 (2020) 43674.
- [3] S. Horike, Q. Wei, K. Kirihara, M. Mukaida, Y. Koshiba, K. Ishida. *Journal of Materials Chemistry C* 9 (2021) 15813.

Thermoelectric properties of ionic materials derived from lignocellulosic biomass residue.

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Ionic thermoelectric materials have been garnering attention in recent years due to their possibilities to convert heat to electricity.¹ This study explores the potential of lignin-based hydrogels as ionic thermoelectric platforms from clean and sustainable resources. The hydrogels were synthesized from a KOH solution, organosolv lignin and PEGDGE as the crosslinker. The thermoelectric properties of these hydrogels were investigated, with an emphasis on the Seebeck coefficient and electrical conductivity, with techniques such as FTIR and SEM being employed for further characterization. Large Seebeck coefficients in the range of 9 to 30.4 mV K⁻¹ were obtained, with electrical conductivities ranging from 0.3 to 5.9 S m⁻¹.

Thermoelectric characterization of the samples indicates that by increasing the electrolyte concentration in the hydrogel increases the Seebeck coefficient, but only to a certain point, from where it starts to decrease. The same occurs when varying the amount of crosslinker in the sample. Similarly, electrical conductivity also increases with both KOH concentration and crosslinker ratio up to a certain point, but the subsequent decrease in electrical conductivity at higher concentrations or crosslinker ratios is drastically higher than the one observed for the Seebeck coefficients. This is supported by the morphological characterization, which revealed a higher degree of crosslinking and a diminishment in porosity of the samples at higher KOH concentrations and crosslinker ratios, contributing to the observed decrease in Seebeck coefficient and electrical conductivity.

The power factor of the samples was calculated from the Seebeck coefficient and electrical conductivity measurements, obtaining values as high as 4187 μW m⁻¹ K⁻², indicating the great potential that these hydrogels have as future sustainable ionic thermoelectric platforms.

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References

[1] Y. He, Q. Zhang, H. Cheng, Y. Liu, Y. Shu, Y. Geng, Y. Zheng, B. Qin, Y. Zhou and S. Chen, *The Journal of Physical Chemistry Letters* 13, 2022, 4621-4627.