Interim Report to the ÅForsk Foundation

Project: 18-351

Title: Printable Ionic Thermoelectric Devices for Self-powered Wearable Sensors

P.I.: Dr. Dan Zhao-860222-9208

Linköpings universitet

Laboratory of Organic Electronics/ITN

601 74 Norrköping

Email address: dan.zhao@liu.se

Summary of the results

The main objective of this project is to develop ionic thermoelectric modules that are suitable for low-cost, large area manufacture. The focuses are discovering and optimizing materials, constructing new device concepts, and demonstrating them in practical applications such as power-suppliers and self-powered temperature sensors. The project is progressing well and we have already obtained positive preliminary results. More specifically, we are able to build first-stage fully-printed thermopiles based on solid and flexible electrolytes, which can generate an extremely large output voltage with small temperature difference. This was achieved by developing a novel ambipolar ionic polymer gel with giant and tunable Seebeck coefficient. We can successfully control the Seebeck coefficient of the gel from negative to positive by adjusting the gel composition. This greatly facilitates the low-cost manufacture of ionic thermoelectric module in large scale, and shows promise for high energy density applications. Our work on this topic was recently accepted to publish on ***Nature Communications*** (with acknowledgement to the ÅForsk foundation), one of the top journals in science. Next steps involve understanding the mechanism of the thermodiffusion and optimization of device geometry to adapt practical applications.

We also explored different possibilities to realize the function of ionic thermoelectric generators as power supplier. Directly utilizing the leaking current and transferring charge to a larger supercapacitor have been preliminarily demonstrated. The tremendous output thermovoltage of the ionic thermoelectric materials plays crucial role in both of the strategies, which cannot be realized by traditional thermoelectric generators. For the self-powered temperature sensor part, we successfully integrated our ionic thermoelectric material with pyroelectric devices, which shows advantages from both effects. In summary, the project is progressing very well and we are eager to continue to investigate the details of the demonstrated devices and to turn them into practical applications.

Results and Discussion

In the project, we proposed to focus on three parts: 1. Ionic thermoelectric materials and device optimization. 2. Ionic thermoelectric power supply for wearable sensors. 3. Power-free thermoelectronic devices for temperature sensing and mapping.

In the section below, the details of how the three parts of work was carried out in the past 7 month are described.

1. Developing new ionic thermoelectric materials: So far, the lack of n-type materials (with negative Seebeck coefficient) and solid state electrolytes are the main limitations for developing ionic thermoelectric modules. In this project, we have focused to develop an “ambipolar” polymer gel with negative Seebeck coefficient and demonstrate that both the sign and the magnitude of the Seebeck coefficient can be controlled by tuning the composition of the polymer matrix. A solid electrolytes compose of ionic liquid and copolymer poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) was explored here as the water-free ionic thermoelectric material (figure 1a). This type of ionic polymer gels are well known as ionic conductors, but their thermoelectric property has never been studied. After testing different ionic liquids, we found out that the combination of ionic liquid 1-ethyl-3-methylimidazolium ([EMIM]) bis(trifluoromethylsulfonyl)imide ([TFSI]) with PVDF-HFP gives us an ideal result. As shown in figure 1b, the polymer gels shows a negative Seebeck coefficient of -4mV/K, which is currently the record of n-type thermoelectric materials. Moreover, this solid gel is very suitable for low-cost screen printing, because the negative Seebeck coefficient can be easily switched to positive by adding small amount of polyethylene glycol (PEG). It is possible to uniformly print all the legs with same polymer gel (n-type), and print PEG into every second legs as shown in figure 2a to switch them into p-type. Figure 2b shows the output voltage of the printed thermopile (photograph shown in figure 2c) with different applied temperature difference (ΔT), as high as 185 mV/K. However, the output voltage did not reach the calculated value (dashed line in figure 2b), that is because we only did the first demonstration without further optimized the ink properties, further study is needed to improve the device performance, including printing on flexible substrates (as shown in figure 3d), size reduction, and electrodes optimization.

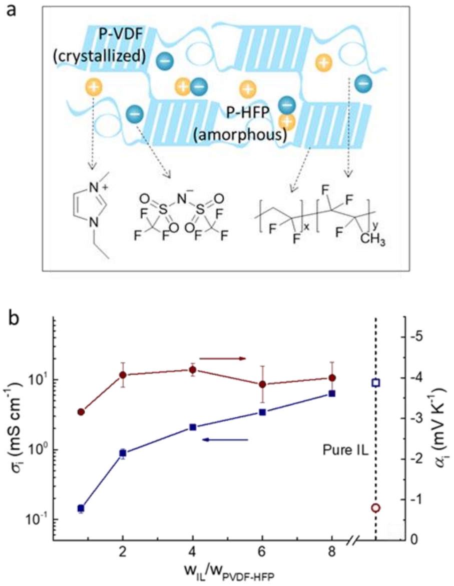

Figure 1. a Schematic illustration of the polymer gel composition. b Ionic conductivity (blue squares) and Seebeck coefficient (red dots) of the polymer gel for different ionic liquid (IL) weight ratio.

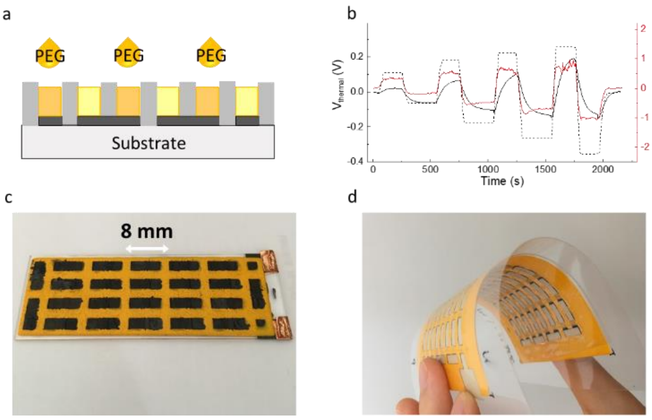

Figure 2. a Illustration of printing ionic thermopile. b Measured (black solid line) and calculated (black dashed line) of the output voltage of the printed device. c and d Photograph of the printed ionic thermopile.

In this project, we started to use pulse field gradient (PFG) nuclear magnetic resonance (NMR) spectroscopy, Raman and infrared spectroscopy to investigate the motion and interaction of ions in the polymer gel, in order to gain information of the ionic thermodiffusion. We are confident that in the year 2 and 3 periods of this project, we will be able to have an overall understanding of the electrolytes with good thermoelectric properties.

In this work, we have discovered a solid electrolyte with large tunable Seebeck coefficient, and preliminary demonstrated the screen printing of the first ionic thermopile based on the novel material. Our pioneer work on ionic thermoelectric materials and applications was recently accepted by ***Nature Communications***. However, there are still a lot of unknown mysteries and room to improve in this topic, we believe that in the next two years of this project, we will have better understanding and more developments.

2. Building ionic thermoelectric power supply: We have started two tracks to realize the goal of using ionic thermoelectric device as the power supplier for practical applications. The first strategy is to directly utilize the leaking current from the ionic thermoelectric generator. We recently discovered that one of the electrolytes we developed, NaOH in PEG solution[1], can generate a stable redox current to the external circuit. The mechanism is similar to thermogalvanic cell (TGC), but here the output thermovoltage is more than 10 times higher than typical TGC for the same temperature difference, which is especially beneficial for applications that require certain voltage level. We preliminarily show that the combination of the leaking current and high output voltage generated by our ionic thermoelectric device can be used to induce chemical reactions. As shown in figure 3a and 3b, the output voltage and current of ionic thermoelectric device were monitored when a temperature difference was applied. At the beginning, only the output voltage (thermovoltage) increased while the current remained at almost 0. Until the output voltage reached 0.27 V, which is the required polymerization potential for our chosen monomer, the current started to increase, and we observed the deposited polymer on the electrode (as shown in figure 3c). The current density can be improved (Au in figure 3a and carbon nanotube in figure 3b) by using different electrode materials, which will be further studied in year 2 and 3 periods of the project.

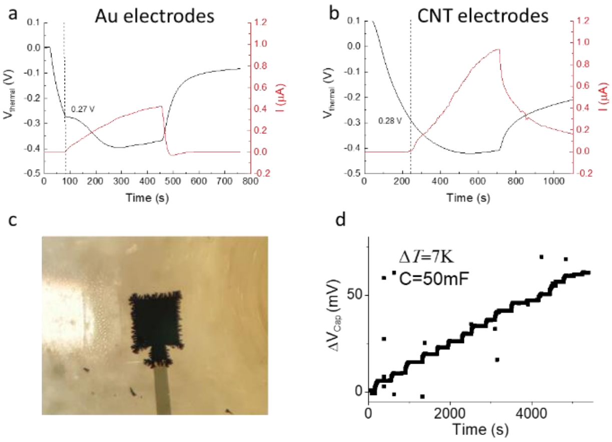

Figure 3. a and b The output voltage and current of ionic thermoelectric generators filled with NaOH-PEG. c Photograph of the polymerized electrode. d Demonstration of accumulating charges from ionic

The second strategy is to build a circuit that can accumulate the charge (energy) generated in the ionic thermoelectric charged supercapacitor (ITESC) we previously reported. We have preliminarily tested to use the IIESC to charge another large commercial supercapacitor. As shown in figure 3d, by applying a fluctuating temperature difference, the ITESC can be charged many times and transfer the charge into the large commercial supercapacitor. As a result, the energy density can be enhanced by approximately the number of charging circles. Benefiting from the high Seebeck coefficient of the ionic thermoelectric materials (11-14 mV/K, more than 50 times large than the best commercial material), the voltage of the large supercapacitor can reach a high value only after a few circles. We plan to further improve this structure by employing a boost circuit, in which a few commercial supercapacitors will be connect in parallel during charging, and connected in series while used as power supplier, in order to maximum the energy transfer as well as obtain a higher output voltage.

Our preliminary results confirms that the extremely high output voltage of our ionic thermoelectric materials can realize uniquely energy conversion which are applicable for other thermal-sensitive materials. In the next two years of this project, we will finalized and optimize these two concepts of high energy density conversion, and demonstrate their function in practical wearable sensors.

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[1] Zhao, D., et al. Ionic thermoelectric supercapacitor, Energy Environ. Sci., 9, 1450-1457 (2016).

3. Developing self-powered wearable sensors: As we discussed in our previous work[2], ionic thermoelectric and pyroelectric devices both has advantages and disadvantages for self-powered temperature sensor applications. In this project, we have preliminary demonstrated an integrated device that composed of both materials and heritages both their advantages. As shown in figure 4 a, a pyroelectric layer can provide quick and large electric output signal when temperature escalates, but the signal is not stable during the heating. While as shown in figure 4b, the ionic thermoelectric layer can generate stable response but the signal is very small and slow compare to the pyroelectric part. After we integrate them, as shown in figure 4c, with the same temperature changing we obtained the quick response of the pyroelectric effect and the stable signal form the ionic thermoelectric part.

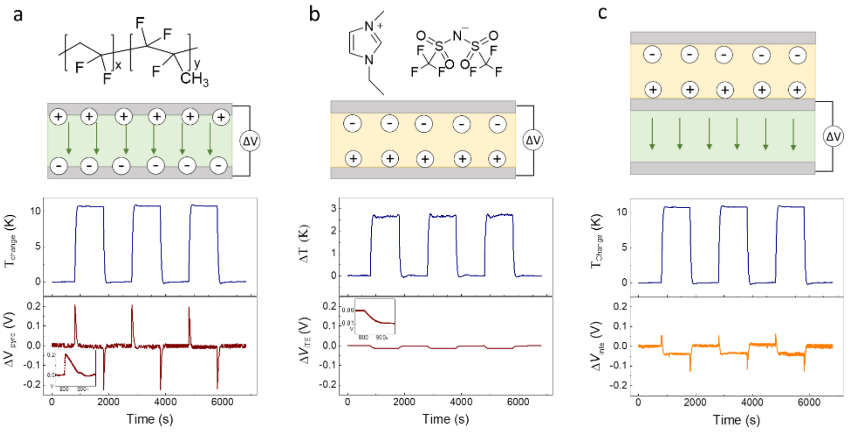

Figure 4. a The illustration and response during heating of the pyroelectric device architecture. b The illustration of the ionic thermoelectrtic device and the thermal voltage response when the bottom substrate is heated. c Schematic illustration of the combined pyroelectric and thermoelectric device and the response of the pyroelectric layer under heating in the same way from the bottom substrate.

It is important to mention that the interaction between the two effects are not simple superposition. We observed an enhancement of the thermoelectric voltage, which has the potential to greatly improve the performance of general thermoelectric generators after systematic study. We are still investigating the possible mechanism that promotes such enhancement.

So far, we have mainly focused on demonstrating that the integrated device is possible to be applied as a power-free temperature sensor. As shown in figure 5, both temporal (peak value) and static (saturated value) of the integrated device are linear with temperature changing. Because the pyroelectric material is also sensitive to pressure, which is one of the main reason that hinders it from applying in wearable sensors. We also tested the tactile response of the device, as shown in figure 5 c and d, it is clear that after integrating with ionic thermoelectric layer, the device is much less sensitive to pressure. **Our results confirm that the integrated ionic thermoeletric and pyroelectric device is cabable to surmount the current problems in self-powered temperature sensors, which opens up novel possibilities in future sensor design**. In the next two

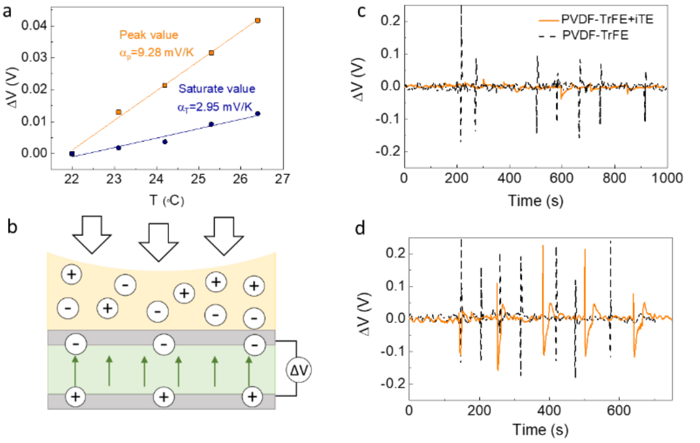

Figure 5. a The temporal (peak value) and static (saturated value) of the integrated device plotted with temperature. b Illustration of the tactile response test. c The response of the pyroelectric device and integrated pyro-iTE device from temporal pressing by plastic c) and by finger d.

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[2] Zhao, D., Fabiano, S., Berggren, M., Crispin, X., Ionic thermoelectric gating organic transistors, Nat. Commun., 8, 14214 (2017).

years of this project, we will devote to understand the physics of the ionic thermovoltage enhancement observed in the integrate device, as well as further optimize the device structure in order to adapt low-cost fabrication.

Next step in the project and future plans

Until now, we have obtained promising results and positive indication of the application of ionic thermoelectric generators in wearable devices. Next steps include understanding of the underlying mechanism of the materials with great thermoelectric properties, optimizing the geometry of the preliminarily tested devices and the manufacture process, and demonstrate their power supply function in practical applications.