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Assembly of Liquid-based thermoelectric generator modules based on amine bonding

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ABSTRACT

In the previous years, it has been shown that ionic liquids (IL) are good candidates as base material for thermo-electric generators (TEG). Having identified promising ILs, the next step is building a module integrating those liquids and enabling its use with consumer devices. To keep the flexibility given by a liquid TEG, all the involved materials must be flexible.

A TEG is composed of three different layers: 1) the bottom electrode foil, 2) a core foil, containing cavities with liquids, and 3) the top electrode foil. The core foil must be flexible, tight, easily shaped and must exhibit a low thermal conductivity. Inspired by microfluidics, polydimethylsiloxane (PDMS) was chosen. The electrode foils have to withstand metal coating and patterning, must be flexible while retaining electrical conductivity, and must not react with the liquids.

Unfortunately, PDMS is not easily bonded to another polymer. Moreover, hermetic sealing of the liquids in a cavity while keeping the contact with the electrode is critical. The TEG being serial connected, if one junction fails the entire TEG fails.

In this paper, we demonstrate a way to create the module first by using amine-based bonding of the liquids-accepting housing, and then filling the core cavities with liquids featuring different Seebeck coefficients, using a home built vacuum chamber. The results on bonding and filling are encouraging; they ensure tightness of all the 100 TEG contacts between ILs and electrodes. A Seebeck coefficient (SE) of $1 \text{ mV}\cdot\text{K}^{-1}$ was measured, which is inferior to the expected value and thus asking for multiple improvements. However, the results must rather be seen as a proof of concept, especially concerning the sealing of the liquid, and as a step in the manufacturing process of highly integrated liquid-containing devices.
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1. Introduction

Previous works showed that ionic liquids (ILs) as thermoelectric material have several advantages over solid-state materials [1,2]. Besides low thermal conductivity (typically $0.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and a substantially increased Seebeck coefficient ($\text{SE} > 1 \text{ mV/K}$) values, ILs allow inherently bendable thermoelectric generator (TEG) designs. Flexibility is especially interesting in the field of “wearables” – devices that can be worn on the body – such as sensors, smart watches, or medical devices. In those conditions, one side of the TEG is in contact with the body, while the other is in contact with ambient air, meaning this kind of TEGs will have to work in a temperature range close to that of the human body.

Naturally, creating a bendable TEG based on liquids requires manufacturing steps to ensure that the liquids are hermetically sealed in their cavities, while conserving electrical contact on opposite sides of the encapsulated wells. However, shunting must be avoided as it would result in the failure of the serial-connected system. Researchers having manipulated liquids at micro-scale are familiar with the facts that 1) having a leak-free device might be difficult, and 2) having liquid enter a recipient of small dimensions and confining the liquid in it is challenging. While those two issues are difficult enough, TEG design dictates other constraints necessary to obtain maximal yield in thermal to electrical conversion. As a TEG needs a temperature gradient across the liquid to function properly, the core material should act as thermal insulator. However, heat transmission is essential at the device-environment interfaces to capture as much thermal energy as possible on one side, and to drain it on the other side. The bendable nature of this

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liquid TEG together with these thermal properties and chemical inertness limits the choice of materials.

In this paper, we present the chosen materials for a bendable, ionic liquid-based TEG, and the different steps necessary for manufacturing such devices. The TEG production should consist of a limited number of easy and accessible steps, keeping in mind a possible upscaling of the process at industrial level. The ILs were measured in a single-cell TEG setup presented in [3], and chosen with respect to their SE values. The result is a proof of concept of a bendable, IL-TEG based on amine-bonding for liquid sealing.

2. Experimental

2.1. Design

For our flexible TEG, a standard serial design was chosen (Fig. 1 left). It consists of three parts: 1) the top electrodes 2) the core and 3) the bottom electrodes (Fig. 1 right). The core contains 100 wells destined to receive two different liquids 1 and 2, having different SE, connected in series via metallic electrodes (500 nm thick sputtered rhodium layers). The dimensions of the core are $38 \text{ mm} \times 38 \text{ mm} \times 1.5 \text{ mm}$. The electrodes are protruding out of the core ($50 \text{ mm} \times 38 \text{ mm} \times 0.05 \text{ mm}$), permitting independent testing of each line of cells. Finally, small holes are cut in the electrodes to allow liquid to fill the cells.

2.2. Materials

The core of the TEG must hold the liquid but needs a low thermal conductivity to maintain the highest temperature gradient between the hot and cold sides. Polydimethylsiloxane (PDMS) is well known in the microfluidics world for its ease of use, tightness and flexibility. With a thermal conductivity of $0.15 \text{ Wm}^{-1} \text{ K}^{-1}$ [4], PDMS stays a good candidate for the TEG core. Sheets of 1.6 mm thick PDMS were used (Superclear Silicone sheet, Silex Ltd, UK).

The electrodes are made of sputtered rhodium on polyethylene terephthalate (PET). PET (Mylar A, Dr. Dietrich Mueller GmbH, Germany), allows flexibility and stability for manipulation at the same time. The reduced thickness of the film compensates the low thermal conductivity of PET and should have minimal influence on the heat transfer from the hot and cold environments to the TEG core itself.

The linker allowing bonding of PET to PDMS is poly(dimethylsiloxane-co-(3-aminopropyl)methylsiloxane) (Merck KGaA, Germany), an amine with a PDMS extremity.

The liquids used to fill the TEG are propylene carbonate (PC) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI TFSI). $\text{Co}^{\text{II}}(\text{bpy})_3(\text{NTf}_2)_2/\text{Co}^{\text{III}}(\text{bpy})_3(\text{NTf}_2)_3$ was added as redox

couple for the current extraction. All liquids came from Merck KGaA, Germany.

Measurements in the single-cell setup yielded the results shown on Table 1:

As seen in [5], SE and current extraction of p- and n-type ionic liquid differs widely, meaning pairing the two results in a mismatch of resistances. Here, two p-type liquids were chosen, where the difference of Seebeck coefficients is small ($0.12 \text{ mV}\cdot\text{K}^{-1}$), but the resistances of the liquids are better matched. With this combination $12 \text{ mV}\cdot\text{K}^{-1}$ could theoretically be reached with the 100 cells of this present TEG.

2.3. TEG manufacturing

Fig. 2 shows the workflow for manufacturing a TEG. The electrodes and the core foils can be processed in parallel. PET sheets are cut using a femtosecond LASER (Pharos PH1-20, Light Conversion UAB, 344 nm) to the exact dimensions, with 1 mm diameter alignment holes and $500 \mu\text{m}$ for later filling. Rhodium is sputtered through LASER-cut alumina shadow masks. The core is mechanically cut with a specially designed jig, where beveled tubes are pressed through the PDMS (Fig. 3).

Based on [6], the amine is uniformly spread on the surface of the PET foils with their contact patterns, left for 20 min at room temperature and then is thoroughly rinsed in a sonicated bath of isopropyl alcohol. The addition of this amine-linker is a necessary step to be able to bond PDMS with PET (Fig. 4).

Both amine-coated PET and PDMS are placed in an alignment jig (Fig. 5 left), and introduced in a vacuum chamber. An oxygen plasma (Plasmaline 415, $2 \cdot 10^{-3} \text{ mbar}$ O_2 partial pressure, 35 s, 50 W at 13.56 MHz) is created to activate all the surfaces. After venting the chamber with nitrogen, the electrodes and core parts are immediately put in contact with a slight pressure, precisely guided by the jig. Afterwards, the whole jig is left for 1 h in an 80°C oven to complete the bonding (Fig. 5 right).

2.4. TEG filling

To have liquids enter into small cavities requires a parallel process, allowing simultaneous filling of one liquid on each side. Vacuum assisted filling is an efficient way to force the liquid inside the holes. For this reason, a small vacuum chamber was designed and built. The bonded TEG is clamped in a metallic frame, ensuring a certain stiffness to the device. ILs are loaded in glass balloons (Fig. 6). Everything is placed in one chamber; all process steps must be carried out without breaking the vacuum. For this reason, an oil-free dry scroll pump was used (reaching $4 \cdot 10^{-2} \text{ mbar}$). After some possible degassing from the liquids, an air plasma is performed (1 min, 30 W) to increase the wettability of IL on PET. In

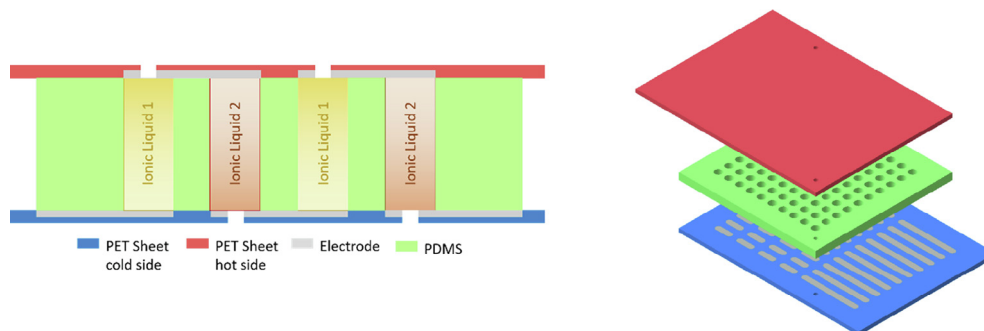


Fig. 1. (Left) Cross-section of the design. (Right) Red: top electrode foil with metallic electrodes (underneath, not visible); green: polymer core with holes for liquids; blue: bottom electrode foil with metallic electrodes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Liquid + 0.01 molL ⁻¹ Co ^{III/III} redox	SE (mV·K ⁻¹)	Power (μW·m ⁻²) ΔT = 30 K	Power (μW·m ⁻²) ΔT = 50 K
Propylene carbonate (PC)	1.76	6191	52,625
PC mixed with 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI TFSI) 1:1	1.64	3554	17,144

the next step, the first IL is spread on the whole upper surface. The chamber is vented rapidly with argon, forcing the liquid into the holes then pumped again. The excess liquid is tipped into a small collecting cup. The TEG is turned 180° and the same procedure is repeated for the second IL (Fig. 7).

The chamber is also fitted with a resistive coil heater, allowing reducing IL viscosity by radiative heating, or for melting such ILs that are solid at room temperature.

2.5. Testing

The TEG was clamped in the setup usually reserved to characterize IL Seebeck coefficient (described in detail in [2]), and a temperature gradient was applied. The cold electrode was maintained at 22 °C and the hot electrode heated up to 55 °C. No further adjustments were made for the present tests.

3. Results and discussion

3.1. PDMS core

Punching holes in the PDMS core is an efficient way to create the future cavities. However, due to the mechanical pressure of the beveled pins, and the flexibility of PDMS, this latter has a tendency to deform, leading to different dimensions for entry and exit holes (Fig. 8). The surface of liquid in contact with the electrode is approximately 110 mm² on the entry side, and 170 mm² on the exit side. As the Seebeck coefficient depends on the surface of electrode in contact with the liquid, this asymmetry could lead to some effect or offset on the measurements. Compressing the PDMS prior to the punching should reduce the asymmetry, as PDMS will not deform during the process.

3.2. Bonding

The bonding process from [6] is straightforward. When bonded, PDMS and PET are irreversibly joined; the attempt to separate the two components leads to the tearing of PDMS, and not delamination at the interface. The main advantage of this method is its sim-

plicity, as no sputtered silicon oxide or other type of material deposition is necessary for the bonding. However, the yield of the bonding is low in our case (0.5), and may be depending on different factors, such as residue or deformation around the PDMS holes due to punching, ambient humidity or the force applied when the PET sheet is pressed against PDMS. When relative humidity in the lab reached 60%, a homemade glovebox filled with nitrogen was used to lower humidity to 20%. It seemed to be beneficial to the process, but was not completely infallible. Concerning the applied pressure, too little and the PET sheet will not lie flat against the PDMS. Too much and the PDMS deforms, and the bonding process is compromised. The force corresponding to a 170 g weight yielded good results.

3.3. Chamber design and IL-filling

The main challenge of vacuum filling is the construction of a chamber where all the accessories needed for this step are included. Generally speaking, liquids and vacuum are a difficult combination. The pressure of the system must allow the ignition of a 13.56 MHz glow-discharge plasma for surface activation (wetting). It must also ensure that despite the very low vapor pressures of the concerned ionic liquids, outgassing of the liquids does not interfere with the process. Moreover, a heating system was added to heat the more viscous – or solid – ionic liquids to reduce viscosity and allow the liquid to enter more easily into the holes.

Different setups were tested, first using syringes to pour the liquids. This did not allow for degassing, and lead to either liquid spraying the interior of the chamber, or leaking off the syringe. Finally, glass balloons connected with 5 mm diameter glass tubes allowed the liquids to degas without contaminating the TEG.

Concerning plasma activation of the surface, the metallic cylindrical electrode serves as both electrode and housing for the thermocoax heating system. In our case, the flexible polymer-based TEG was deformed if plasma activation exceeded 70 W for 1 min. The generated heat caused the TEG deformation.

Pouring the ILs went well, but the liquid needs a barrier to stay on the surface. A small metallic frame holding the TEG was included for two purposes: to rigidify the assembly for easier handling, and to act as a barrier for the liquids. The tests without this frame led to incomplete filling of the holes.

The holes were completely and accurately filled with ILs when argon was rapidly introduced in the chamber by opening a valve. The pressure over the liquid increased from 4·10⁻² mbar to atmospheric pressure in a fraction of a second, pushing the liquid in the holes. If a bubble is trapped, it is possible to repeat the procedure (vacuum and venting) to remove it. Once the liquid enters the PDMS cavities, it is difficult to remove it. Therefore, the surface of the TEG can be cleaned by simply wiping the excess liquid on the surface. For added safety, the holes were sealed with regular office adhesive tape.

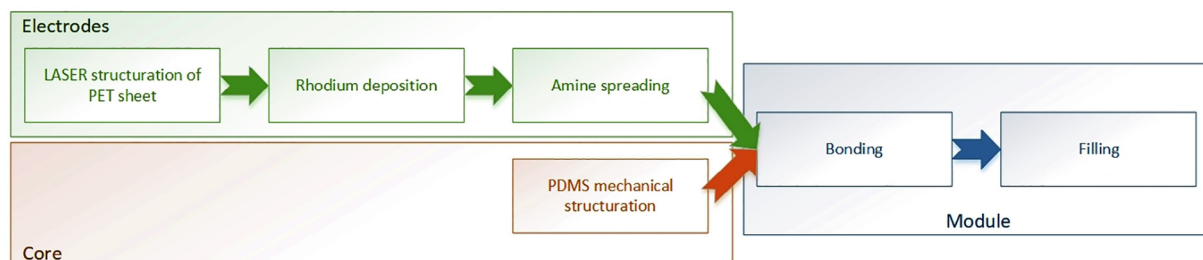


Fig. 2. Workflow for flexible TEG production. Electrodes and core foils can be produced in parallel, followed by the bonding and filling with ionic liquids. Few steps are required and easily up-scalable.



Fig. 3. Close-up of beveled pins used to punch holes through the PDMS core.

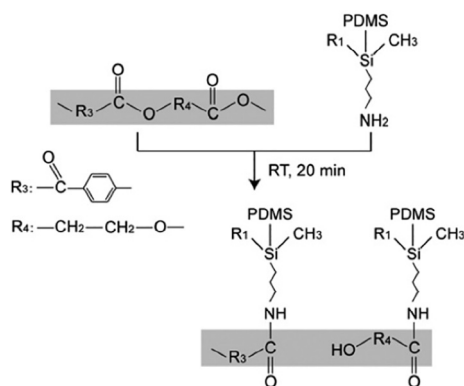


Fig. 4. Working principle of amine bonding: The amine group is grafted selectively to the PET surface, and the PDMS tail can then be bonded to another surface with a standard procedure, such as plasma-induced activation [6].

3.4. Testing

Electrical connectivity was tested by contacting rhodium electrodes with alligator clips on both ends of the TEG. A signal was measured, meaning that all the 100 cells were effectively connected in series. This is already a major achievement, as one under-filled cell where the liquid does not touch the rhodium electrode is

enough to cut the connectivity and reduce the total efficiency of the TEG.

When a temperature gradient is applied, measurement of a Seebeck coefficient is possible. Fig. 9 shows the measured voltage with respect to the temperature difference. This kind of measurements was performed on two different TEGs, with similar results. A Seebeck coefficient of $1 \text{ mV}\cdot\text{K}^{-1}$ was measured, significantly below the expected $12 \text{ mV}\cdot\text{K}^{-1}$ of the test cell. Different reasons can explain this inferior value. Our TEG is clamped between two metallic blocs, one heated and the second cooled. The temperature is measured in those blocs. It is then possible that the heat transfer between the heating and cooling elements and the electrodes is not optimal due to the PET sheet, reducing the gradient. It is also possible that the small (1.6 mm) thickness of the core cannot keep the whole gradient due to the thermal conductivity of the PDMS, compared to that of the test cell setup (bigger, and with more thermal insulating materials). Therefore, the temperature gradient would be smaller, generating less voltage.

Moreover, an offset of 30 mV was observed. Due to the yet mostly manual process, the electrodes surface is not equal between the hot and cool side. This unbalance could explain a bigger accumulation of charges on one side of the device, thus creating an electrical offset. This behavior is reproducible, and must be further investigated.

Finally, the high internal resistance of the device yielded low power output. This resistance is very likely coming from the deposition process of rhodium on a polymer, and the process will be modified to decrease it, therefore gaining power. The 100 serial connections, each representing a liquid-electrode interface also play a major role in increasing the resistance.

4. Conclusion

The fabrication process of a flexible, ionic liquid based-TEG was described. The TEG is made of two PET sheets with sputtered rhodium electrodes bonded to PDMS with the help of an amine linker. Hundred cells were connected in series with propylene carbonate as one liquid, and propylene carbonate mixed with 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI TFSI) in a 1:1 ratio as the second liquid. To fill the TEG, a specially designed vacuum chamber was constructed. A primary vacuum was made, then the liquids were poured on the surface of the TEG. By venting the chamber, the liquids entered the cavities in contact with the electrodes. An electrical contact was measured between the two ends of the TEG throughout all 100 junctions, meaning all cavities were successfully bonded and filled. This is a significant result as dealing with liquid encapsulation is always dif-

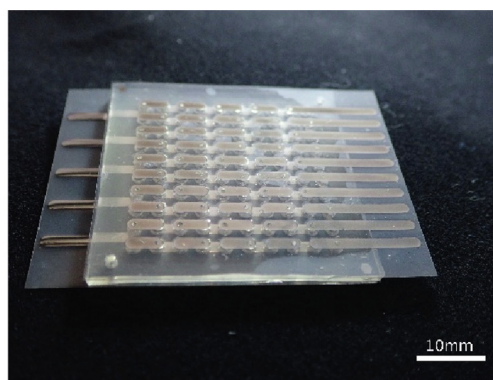
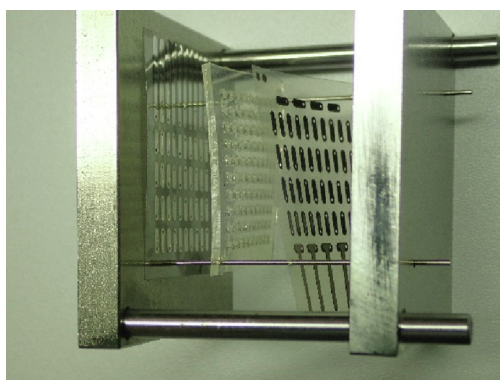


Fig. 5. (Left) Alignment jig loaded with both electrode foils and PDMS core. The whole device is placed in a vacuum chamber for plasma activation prior to bonding. (Right) Bonded TEG with bottom- and top-foils electrodes protruding from PDMS core foil.

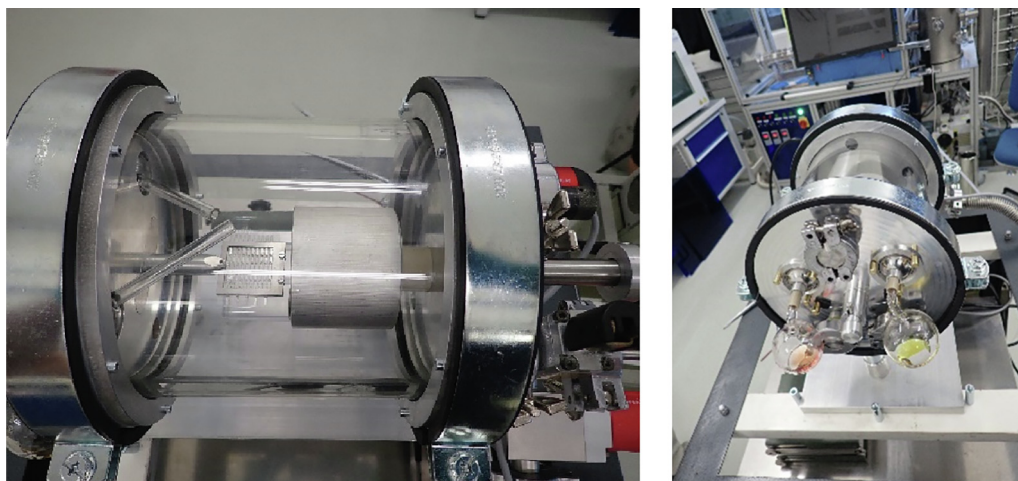


Fig. 6. (Left) Vacuum chamber with clamped TEG in a metallic frame for rigidity. (Right) Left view of the chamber, with glass balloons containing the two different ILs. The balloons allow degassing of the liquids without overflowing.

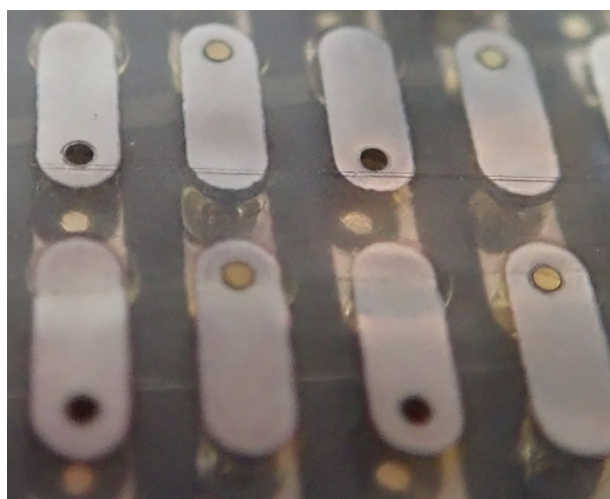


Fig. 7. Close-up of filled cavities. The yellow tint indicates the liquid entered the holes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

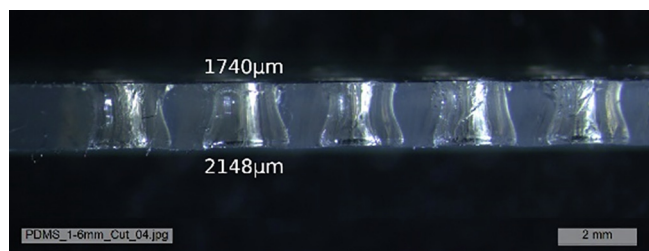


Fig. 8. Asymmetry in the punched PDMS-core. Entry hole is smaller than exit hole.

difficult. A Seebeck coefficient was measured when a temperature difference up to approximately 30 K was applied (between 273 K and 325 K for the hot side). At present, the value of SE is below our expectations ($1 \text{ mV}\cdot\text{K}^{-1}$), possibly due to thermal discrepancies between the measured and TEG in-situ temperatures. An appearing offset of 30 mV is attributed to the electrodes size difference, differently charging the hot and cool side of the TEG. Moreover, the high internal resistance of the TEG limited the power output. Ways to improve the prototypes include further analysis on the

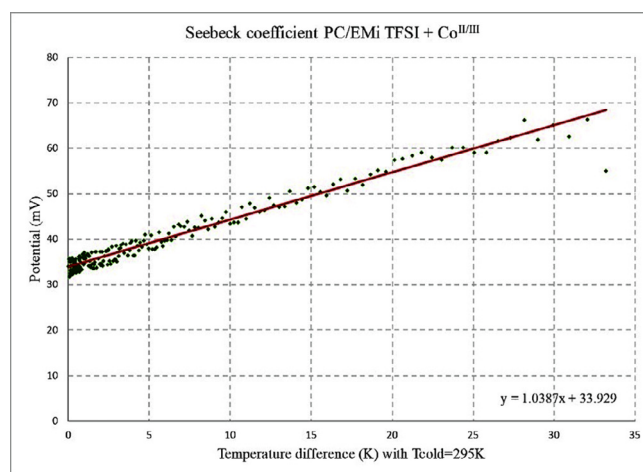


Fig. 9. Measurements of voltage with respect to temperature difference. Seebeck coefficient corresponds to the slope and is here approximately equal to $1 \text{ mV}\cdot\text{K}^{-1}$.

electrodes surfaces and electrical behavior, as well as the possible interactions at the IL-electrode interfaces. Thermal leaks and deviation between the temperature measurement and the real in-situ temperature must also be investigated.

CRediT authorship contribution statement

Laure Jeandupeux: Conceptualization, Investigation, Supervision, Writing - original draft. **Edith Laux:** Conceptualization, Investigation, Supervision, Writing - original draft. **Claudio Prieur:** Conceptualization, Resources, Investigation. **Philippe Potty:** Project administration, Conceptualization. **Herbert Keppner:** Funding acquisition, Conceptualization, Investigation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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