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Progress and perspectives in thermoelectric generators for waste-heat recovery and space applications

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ABSTRACT

The direct conversion of thermal energy into electrical current via thermoelectric (TE) effects rely on the successful integration of efficient TE materials into thermoelectric generators (TEGs) with optimized characteristics to ensure either optimum output power density or conversion efficiency. Successfully employed for powering deep-space probes and extraterrestrial rovers since the 1960s, the development of this technology for waste-heat-harvesting applications faces several key issues related to the high temperatures and oxidizing conditions these devices are subjected to. This Perspective provides a brief overview of some prospective thermoelectric materials/technology for use in Radioisotope Thermoelectric Generators (RTGs) utilized in space missions and highlights the progress made in the field over the last years in the fabrication of TEGs. In particular, we emphasize recent developments that enable to achieve increased power densities, thereby opening up novel research directions for mid-range-temperature applications. In addition to showing how using lower quantities of TE materials may be achieved without sacrificing device performance, we provide an outlook of

the challenges and open questions that remain to be addressed to make this technology economically and technologically viable in everyday-life environments.

I. INTRODUCTION AND BACKGROUND

The development of advanced thermoelectric (TE) materials and devices for power generation (Seebeck effect) and solid-state cooling (Peltier effect) applications is a major challenge in materials science.¹⁻³ This versatile technology enables to harvest waste-heat over a wide range of temperatures from room up to very high temperatures (> 1200 K), providing an interesting solution to power electronic devices under extreme environments in various industrial areas.^{4,5} Although Radioisotope Thermoelectric Generators (RTGs) have been successfully used for several decades as power sources for deep-space probes and Mars rovers,^{1,6} this technology is however still confined to niche applications on Earth due to the technological barriers that must be lifted. Not only do they concern the TE materials themselves, by finding unconventional compounds that combine characteristics of thermal insulators and electrical conductors,^{1-3,7,8} but also their integration into TE devices using well-mastered processes to exploit the full potential of the optimized TE materials.^{4,5,9-11}

With a wealth of strategies designed over the last three decades, the thermoelectric performance of various families of novel materials has slowly, yet steadily been increased, surpassing those of state-of-the-art TE compounds developed in the 60s and 70s and integrated in RTGs.^{1-3,7,8,12} These advances are quantified through the dimensionless thermoelectric figure of merit $ZT = \alpha^2 T / \rho (\kappa_{el} + \kappa_{ph})$ where T is the absolute temperature, α is the thermopower (or Seebeck coefficient), ρ is the electrical resistivity, κ_{el} is the contribution of the charge carriers to the thermal conductivity and κ_{ph} is the contribution of the lattice vibrations.¹⁻³ While state-of-the-art TE materials have for long exhibited ZT values on the order of unity, novel

theoretical ideas have pushed these values to between 1.5 and 2.0 at high temperatures in several families of materials that notably include skutterudites (SKDs),^{13,14} half-Heuslers (HHs),^{15,16} Zintl phases¹⁷⁻¹⁹ and novel chalcogenide semiconductors.²⁰⁻²² Band-structure-engineering tools (resonant levels, band convergence...), nanostructuring or loosely-bound atoms in open-like crystalline frameworks are just few examples of the design principles used for optimization or guidance that proved to be effective in improving the electronic properties or lowering the heat transport.²³⁻³⁶ However, despite these successes, the integration of these novel materials into thermoelectric generators (TEGs) have not kept pace. This is notably due to several key issues that need to be solved to ensure the chemical, thermal and mechanical stability of the devices over long periods of time. Although they were successfully overcome for space applications, most of them still require to engineer solutions to make thermoelectricity a technically- and economically-viable energy-conversion technology in large-scale applications.

In this perspective article, we will focus on the current status of the developments of TE technology for potential use in the next-generation RTGs and on the progress made in the integration of optimized TE materials in TEGs for mid-temperature-range, waste-heat-harvesting applications. Of note, we will not discuss the various strategies used to optimize the TE properties of important classes of materials, as these aspects have been covered in several excellent handbooks and reviews,^{1,7,8} to focus exclusively on TE devices. In addition to the presentation of the two leading technologies for RTGs, we will describe one appealing strategy that enables to concomitantly lower the amount of TE materials integrated and increase the power density of TEGs. This approach, recently applied to skutterudites, fills the gap between TE devices used in solid-state cooling applications near room-temperature and conventional TEGs for power generation. The results will be discussed with an eye towards remaining issues that will need to be tackled in future studies for a wider deployment of this technology on Earth.

II. THERMOELECTRIC GENERATORS: FROM EARTH TO SPACE APPLICATIONS

The conventional architecture of TEGs is made of parallelepiped n - and p -type thermoelectric legs forming a “ π ”, sandwiched by two electrically-insulating and thermally-conducting ceramic plates (AlN, Al₂O₃...) (Fig. 1).

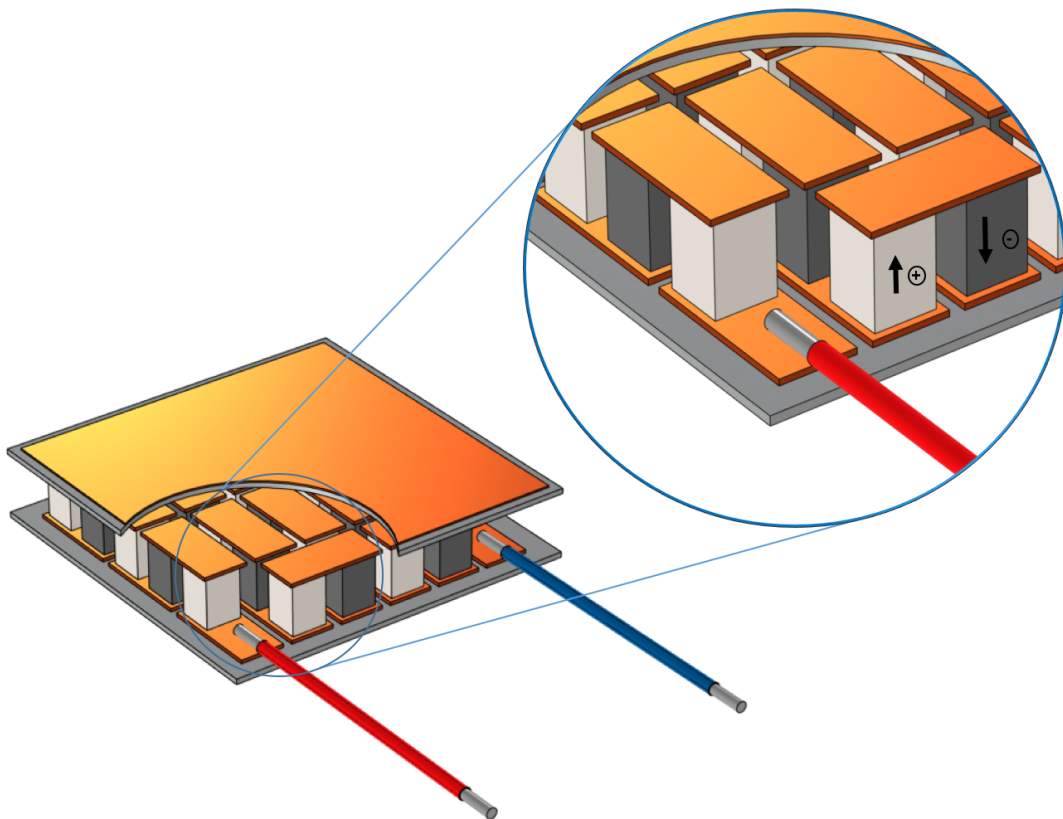


FIG 1. Conventional π -shaped configuration of a TEG composed of p - and n -type TE materials connected electrically in series by metallic electrodes, and thermally in parallel by two ceramic plates (here, the top surface is covered by a metallic coating).

This π -shaped configuration, where both the heat flux and current density are parallel, can also be found in segmented or cascade modules (Fig. 2).¹⁻³ These two alternative configurations have been proposed to reconcile the fact that the highest performance of TE materials is usually

achieved over a narrow temperature range with the necessity to have an applied temperature difference as large as possible between the two sides of a TEG to maximize the conversion efficiency or the output power. Cascade architectures (Fig. 2a) aim at achieving a similar goal but offers more flexibility regarding the choice of the TE materials and induce less interface issues. Segmented legs (Fig. 2b) consist of several TE materials, the performance of which is optimized over the temperature gradient they are subjected to.

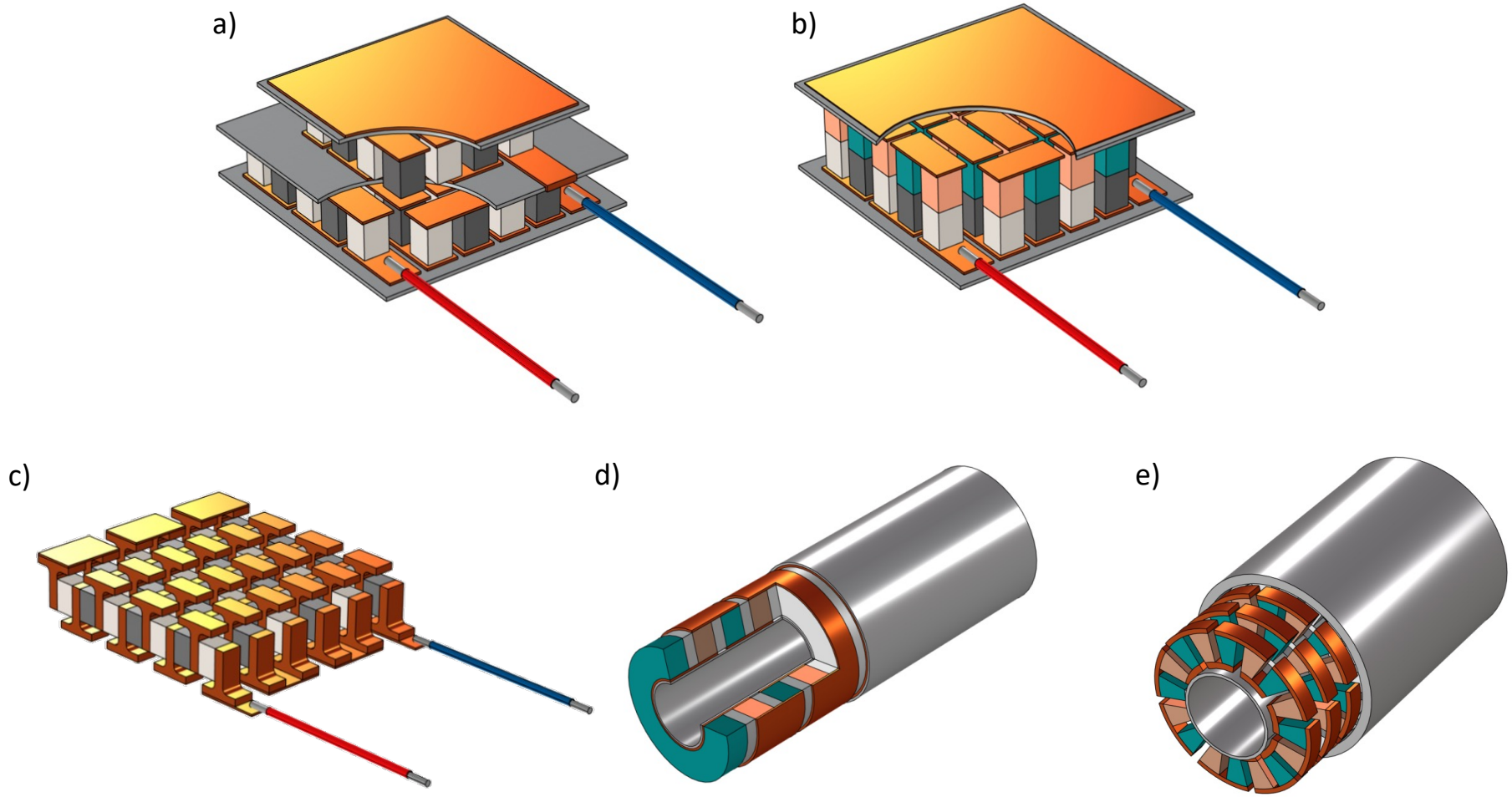


FIG 2. Alternative architecture of TEGs: a) in cascade where both TEGs are thermally connected in series, b) with segmented legs (electrically and thermally connected as in a conventional TEG) consisting of two or more TE materials forming the n - and p -type legs and c) in “Y” shape with metallic electrodes between the n - and p -type TE materials (current flows perpendicular to the vertical heat flux). (For a), b) and c), it is assumed

that the top and bottom ceramic plates are covered by a metallic layer to minimize the thermal contact resistance). Panels d) and e) show two architectures of RTGs for which the TE materials are connected electrically in series, with the heat flowing radially outward.

A fourth configuration in “Y” can be adopted (Fig. 2c), which eases the integration of TE materials with different thicknesses, surface areas and provides additional benefits in efficiently managing the mismatch between thermal expansion coefficients. Each TE element is sandwiched by metallic electrodes forming a Y-shape geometry. With these electrodes that improves the heat transfer between them and the heat source, the electrical current flows from one TE element to another. In this configuration, the current flows perpendicular to the heat flux, enabling the integration of TE materials with various geometries.

Peltier modules used in solid-state cooling applications are usually fabricated with a π -shaped architecture.¹⁻³ In most cases, these modules are used near room temperature, with temperature differences applied between the hot and cold side not exceeding 100 K with a single stage configuration. In such conditions, the thermal stability of the TE materials and the thermomechanical stresses they undergo are not severe issues. For these reasons, and because the cooling power can be optimized by decreasing the length of the TE legs, modules with short legs (from few millimeters down to several hundreds of microns) can be manufactured without compromising their mechanical integrity over time. Bi₂Te₃-based alloys remain nowadays the best TE materials for solid-state cooling,¹⁻³ with the Zintl alloys Mg₃Bi_{2-x}Sb_x emerging as possible candidates to replace them.^{37,38}

In contrast, power-generation applications typically target to harvest waste heat produced at high temperatures, resulting in temperature differences of several hundreds of Kelvin. In addition to the transport properties of the TE materials, issues related to their thermal stability are no longer negligible and represent the main bottleneck to be resolved for a large-scale deployment of TEGs. In industrial applications where the available waste heat is virtually infinite, the output power P , rather than the conversion efficiency, is the main parameter to optimize. Like in Peltier modules, reducing the length of the legs L is also beneficial to increase

the maximum output power P_{max} generated by the TEG according to the following relationship^{1,4,39-43}

$$P_{max} = \frac{(\alpha_p - \alpha_n)^2 \Delta T^2}{4R} = \frac{A(\alpha_p - \alpha_n)^2 \Delta T^2}{4L(\rho_n + \rho_p)} \quad (1)$$

where α_i and ρ_i are the thermopower and electrical resistivity of the leg $i = n, p$, respectively, $R = \frac{L(\rho_n + \rho_p)}{A}$ is the internal resistance of the thermocouple, and L is the length of the n - and p -type legs. This simplest form of P_{max} , obtained assuming temperature-independent transport properties of the TE materials, is strictly valid for a fixed temperature difference ΔT and a matching of the electrical impedance.

As illustrated in Figure 3, the overall variation in P_{max} with L is non-monotonous, with an optimum length that maximizes P_{max} , depending on the power factor of the materials and their thermal conductivity. However, while seemingly simple, this approach leads to several challenges that must be solved to make this solution practicable. Firstly, one of the main issues is the significant increase in the thermomechanical stresses that results from the larger temperature gradients applied. Because the majority of TE materials behave mechanically as ceramics and are thus brittle, the level of stresses can rapidly cross the elastic limit upon decreasing L , ultimately leading to the failure of the legs. A second issue, common to all TEGs operating at high temperatures, is tied to the thermal stability of the TE materials. While nearly all the efficient TE materials discovered so far easily oxidize under oxidizing atmospheres, most of them are composed of volatile elements that can sublime at moderate temperatures. Finally, high temperatures also trigger interdiffusion of the elements composing the TE materials towards the metallic electrodes usually made of metals (Cu or Mo for example). The lack of

thermal stability inevitably degrades the output performance of the TEGs, thereby severely limiting their lifetime.

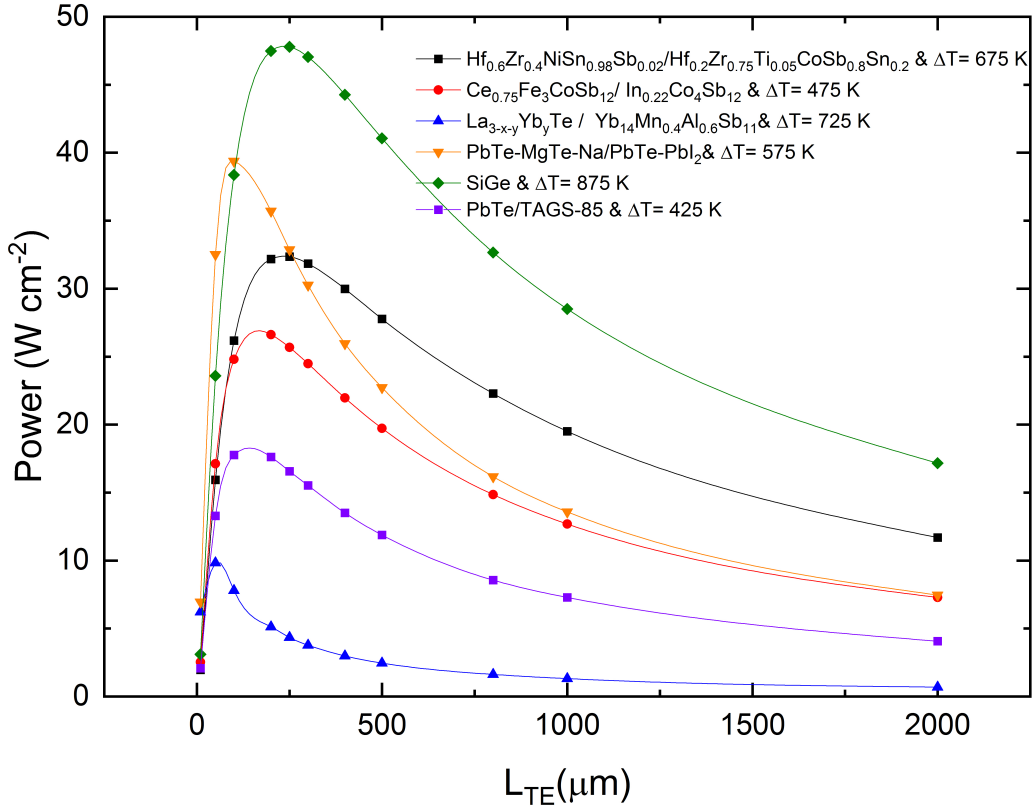


FIG 3. Output power calculated as a function of the length of the TE legs for a single couple made of various TE materials.^{39,44-49} The temperature difference considered in these calculations are indicated.

We recently demonstrated that the first issue can be overcome by inserting metallic composites on either side of the TE materials.³⁹ Being electrically conducting, they neither participate to the generation of the output power nor do they prevent current flow. However, these additional layers help to limit the stresses undergone by the TE materials and hence, act as buffers from a mechanical point of view. Using skutterudites (SKDs) as an example of the active TE materials, we showed that mechanically-robust *n*- and *p*-type legs can be fabricated within only one single step by spark plasma sintering.³⁹ Subsequent measurements of the electrical properties of these legs confirmed low contact electrical resistance at the interface

between the metallic composites and the SKDs, an essential requirement to achieve high thermoelectric performance. Measurements of the performance of the modules fabricated with these legs confirmed that they can withstand large applied temperature differences of up to 630 K.

In addition to being electrically conductive, the nature of the metallic composites must obey another rule: their chemical composition should be carefully adapted so that their thermal expansion coefficients (TECs) match those of the TE materials. If this condition is not fulfilled, the thermal expansion undergone by the TE materials at high temperatures will lead to strong thermomechanical stresses at the interface and will jeopardize the mechanical integrity of the legs. Since *n*- and *p*-type SKDs exhibit different TECs, the composition of the metallic layers has to be specifically adapted. For these reasons, Cu-Ti and Cu-Ag composites were chosen as a proof of concept.³⁹

Another interesting aspect of the presence of these composites is the ease in brazing the TE legs to the metallic electrodes due to their metallic nature. Brazing a metal with another metal is usually easier than brazing a metal with a ceramic due to differences in their respective wettability. Furthermore, the possibility to utilize these TEGs at mid-range temperatures, due to their higher output power, overcomes the delicate problem of finding a suitable braze for this final, yet critical step in the fabrication process of the TEG. While many solders and brazes are commercially available for applications below 400°C (soft solders) and above 600°C (braze alloys), only few are available in between, despite being a relevant temperature range for many industrial applications. In this regard, identifying novel brazes for this particular temperature range would be desirable.

From a practical point of view, studying the aging behavior of the TE legs is essential to assess their lifetime. In particular, the growth rate of intermetallic phases that form at the interface between the SKDs and the metallic layers will determine the evolution of the electrical

contact resistance of the legs over time. This quantity is a key parameter that must be as low as possible to maintain the output performance of the device. For both Cu-Ti and Cu-Ag,³⁹ intermetallic phases form locally within the composite layers due to the numerous binaries that exist in both phase diagrams. However, other combinations of two or more immiscible elements would help to avoid the possible impact of the growth of these phases at high temperatures.

Once optimized, fabricated and protected against thermal stability issues, two other challenges remain: **i)** the integration of the TEGs in their operating environment, notably coupling the TEG to the hot and cold sources, and **ii)** the external electronic system to track the maximum power point and ensure optimal power generation under varying environmental conditions. Regarding **i)**, a moderate/good thermal coupling can be realized by using thermal pastes or by applying pressure. The quality of the thermal contact is a fundamental issue because the added thermal resistance can degrade drastically the output performance of the TEG due to the decrease in the temperature difference ΔT undergone by the TE materials. In many applications, heat exchangers are used to transfer the heat received from the hot source and to reject the non-converted heat at the cold side. The efficiency of these exchangers, characterized by an exchange heat coefficient, further decreases ΔT . The dimensions of the heat exchangers and their architectures represent additional constraints that must be taken into account to globally assess the output performance of the entire system. For the second point **ii)**, it is important to note that the output voltage of a TEG is small and often fluctuates over time when the regime is non-stationary. For this reason, an electrical DC-DC or DC-AC converter must be developed, the role of which is to increase the output voltage delivered by the TEG to fulfill the requirements of the system (impedance) to be electrically powered. The precise control of the converter can be ensured electronically using an optimized algorithm, also used for solar cells, that tracks the maximum power point.

III. RADIOISOTOPE THERMOELECTRIC GENERATORS FOR SPACE APPLICATIONS

Of the various static energy conversion technologies considered for Radioisotope Power Systems (RPS) for space applications, TE energy conversion has received the most interest. RTGs generate electrical power by converting the heat released from the nuclear decay of radioactive isotopes (typically plutonium-238) into electricity using a TE converter. RTGs have been successfully used to power a number of US space missions, including the Apollo lunar missions, the Viking Mars landers, Pioneers 10 and 11, and the Voyager, Ulysses, Galileo, Cassini outer-planet spacecrafts, and more recently the Mars Science Laboratory (MSL) and Mars 2020 rovers on Mars. These generators have demonstrated their reliability over extended period of time (tens of years) and are compact, rugged, radiation resistant, scalable, and produce no noise, vibration or torque during operation. These properties have made RTGs suitable for autonomous missions in the extreme environments of deep space and on planetary surfaces.

Two types of RTGs have been flown on NASA missions, the General-Purpose Heat Source-RTG (GPHS-RTG)⁵⁰ and the Multi-Mission-RTG (MMRTG)^{51,52}. The TE couples used in these RTGs are based on two different types of TE materials. PbTe-based and TAGS (Te-Ag-Ge-Sb-based compounds) TE materials have been used in the SNAP-19 generators and more recently in the MMRTG generators. SiGe-based TE materials have been used in the Multi-Hundred Watt (MHW) and the GPHS-RTG generators. The system conversion efficiency for state-of-practice RTGs is about 6%. Advanced RTGs with higher performance TE technology could be of interest for some potential future NASA missions. In this Perspective, we highlight two types of advanced TE technology under development at the Jet Propulsion Laboratory that could potentially result in higher-performance RTGs in the future.

The concept of a skutterudite (SKD)-based Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) was first proposed in 2013. It is based on retrofitting the flight-proven MMRTG that uses spring-loaded PbTe/TAGS thermoelectric couples with higher-efficiency thermoelectric couples based on SKDs developed at NASA's Jet Propulsion Laboratory (JPL) while keeping the balance of the system virtually unchanged. A multi-organization team composed of Teledyne Energy Systems Inc. (TESI), Aerojet Rocketdyne, the Department of Energy's Idaho National Laboratory, the NASA Radioisotope Power System Program office, and JPL have collaborated to develop and mature the SKD-based thermoelectric converter technology. The purpose is to establish the potential of the SKD-MMRTG to deliver a minimum of 77 We after 17 years of operation (*i.e.*, 3 years under storage conditions and 14 years of operation) or greater than a 30% increase in power from the MMRTG at the same operating conditions. The SKD couple design was finalized in its flight-like configuration in 2020 and an unprecedented amount of verification testing has been accumulated since. Manufacturing has been demonstrated with the fabrication of couples and the 48-couple module and subsequently life tested at TESI and at JPL with up to 3 years of life test data collected to date. More details about the SKD-MMRTG design concept have been previously reported.⁵³

This section provides an update to the couple life test data acquired to date for the flight-like SKD-based couples and the current 17-year life performance prediction best estimate previously reported.⁵³ Over the course of the last several years, the project team has conducted several couple development cycles including fabrication and testing to arrive at the current flight-like configuration. These SKD-based couples are shown in Figure 4. In collaboration with JPL, TESI has demonstrated that they can manufacture these couples with a sufficient yield to support the potential production of a full SKD-MMRTG unit within a similar timeframe as the MMRTG. Beginning-of-life (BOL) performance test data for the SKD-couples demonstrate excellent agreement within a few percent of the predicted values.



FIG 4. TESI-produced flight-like SKD-based couples.

Figures 5 through 7 show the p -type leg, n -type leg and couple peak power for several couples produced by TESI and tested by JPL. The test temperatures shown correspond to a nominal temperature of about 575°C at beginning-of-life (BOL) (at the following conditions: $T_{\text{fr}} = 157^{\circ}\text{C}$, $Q_{\text{BOL}} = 1952 \text{ W}$, and $V_{\text{load}} = 34 \text{ V}$; these are the operating conditions at which the 17-year 77We requirement needs to be met) down to 550°C , with an expected decrease in the couple hot-junction temperature by over 30°C over 17 years. The couples are designed never to operate at a hot-junction exceeding 600°C . An unprecedented 26,000 hours (~ 3 years) of life test data have been acquired to date on the SKD couples. The couple-level data is used to extract the key degradation parameters used as input to the generator-level life performance prediction model, which was described elsewhere.⁵⁴ The couple n -type leg produces $\sim 2/3$ rd of the couple power. Its peak power exhibits acceptable, minimal degradation after ~ 3 years of testing. The p -type leg degradation is slightly higher than the n -type leg but acceptable to meet the End-of-Design Life (EODL) requirement. As typical with any TE during its initial “burn-in” period, the early degradation rate appears to be higher but decreases significantly over time. This is similar to RTGs that have been flown using SiGe or PbTe/TAGS TE materials.

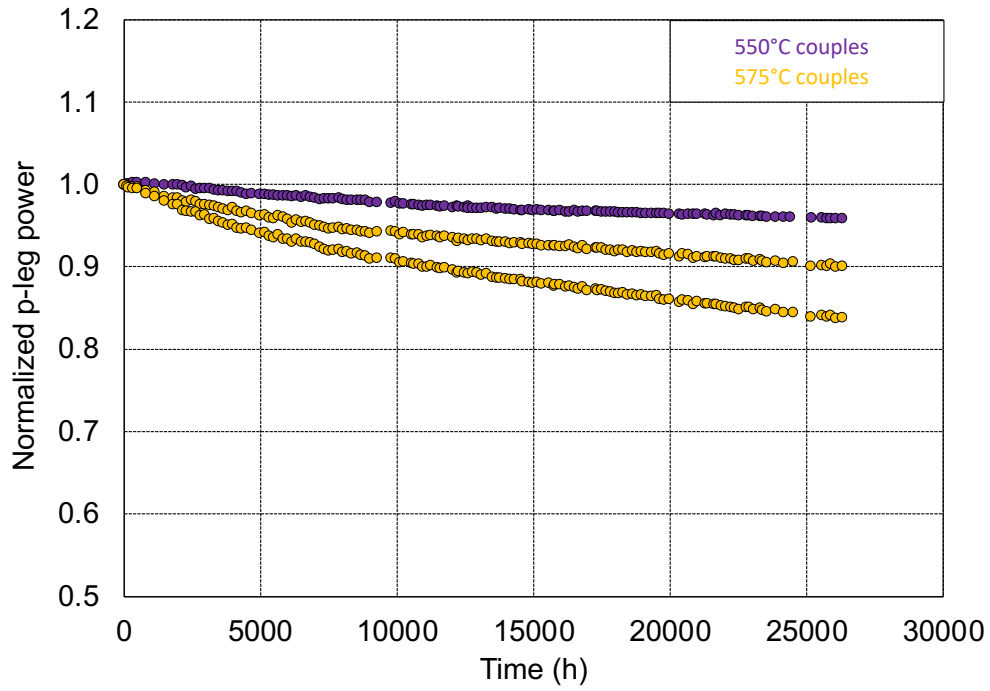


FIG 5. Relative p -type leg peak power as a function of time for several SKD-based couples at 550 and 575°C. The experimental uncertainty is estimated to be ~5%.

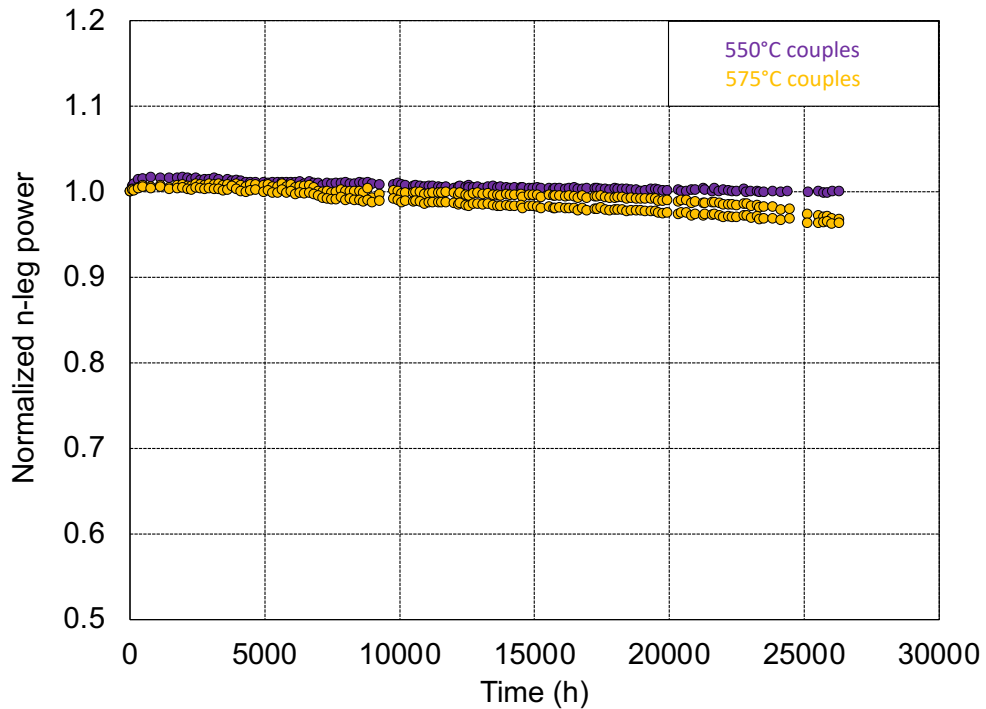


FIG 6. Relative n -type leg peak power as a function of time for several SKD-based couples at 550 and 575°C. The experimental uncertainty is estimated to be ~5%.

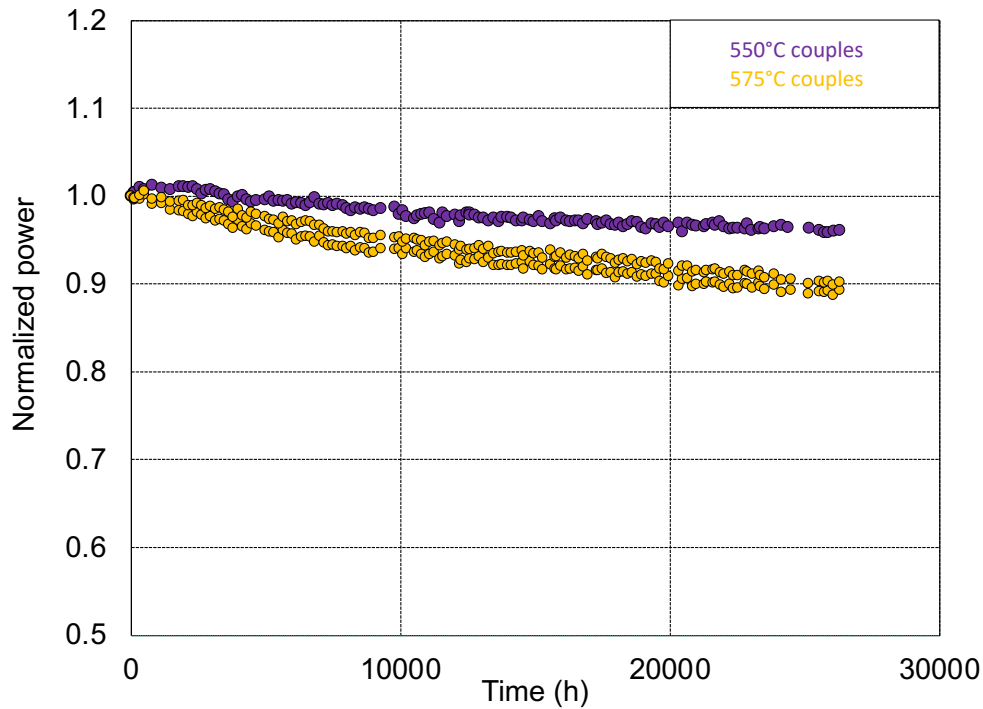


FIG 7. Relative couple peak power as a function of time for several SKD-based couples at a hot-junction of 550 and 575°C. The experimental uncertainty is estimated to be ~5%.

TESI has fabricated a SKD 48-couple module that is plug-and-play compatible with the MMRTG,⁵³ shown in Figure 8. The 48-couple module measured and predicted power output is shown in Figure 9. The measured data is in excellent agreement with the prediction with up to ~ 12,000 hours of data. The 48-couple module, a building block of the generator, is more prototypic and, as such, has less instrumentation. It does not generate input to the physics-based life performance prediction model,⁵⁴ but serves as an initial verification of the life performance prediction at a higher assembly level than a couple alone.

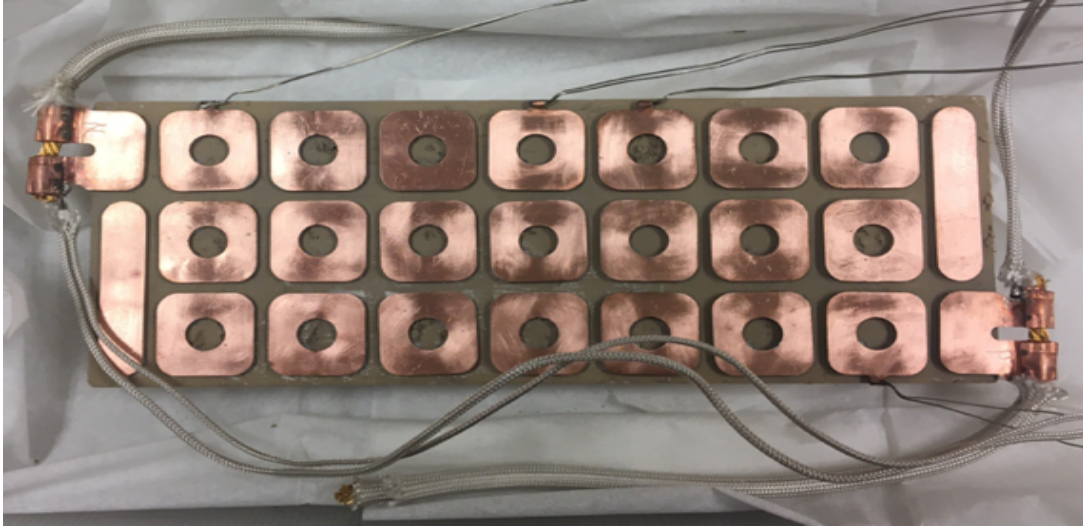


FIG 8. SKD 48-couple module fabricated by TESI.

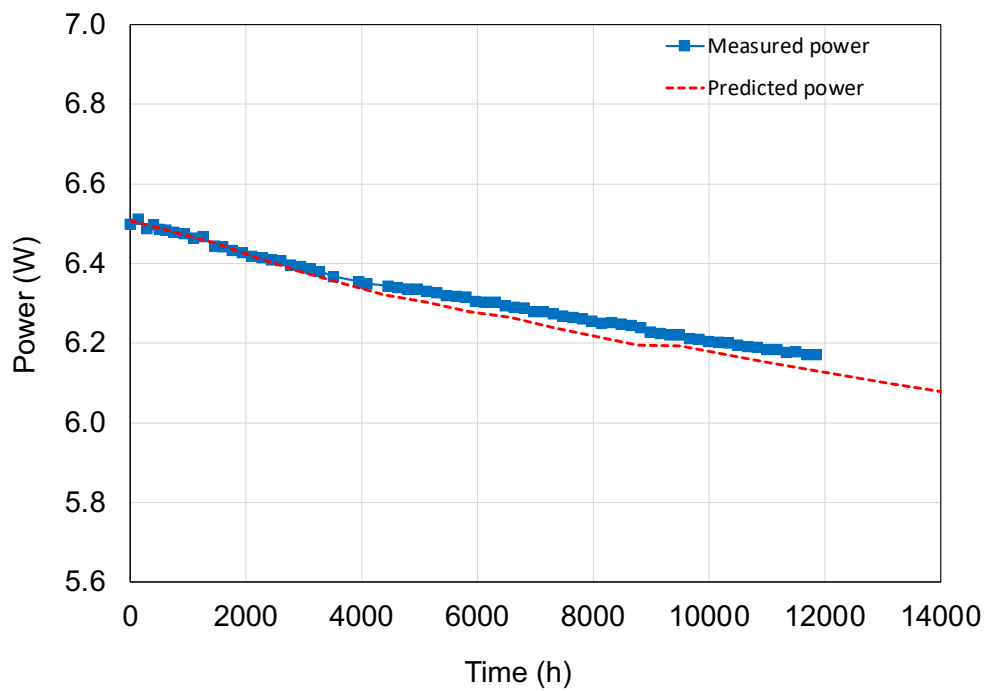


FIG 9. Measured and predicted power values for the SKD 48-couple module are in excellent agreement. The experimental uncertainty is estimated to be ~5%.

Up to 2 uninterrupted years of SKD TE materials TE property life testing has been conducted to date, and the results show that TE properties of SKDs remain unchanged over

time at temperatures ranging from 550 to 650°C. Destructive Physical Analysis (DPA) allowing microscopic inspection and property measurements of several couples tested at temperatures ranging from 550 to 600°C and for different durations have shown that the key degradation mechanism controlling the degradation of the *p*-type legs, and to a much lesser extent of the *n*-type legs, is the degradation of the couple hot-side interfaces between the SKD materials and the metallization adjacent to them. The degradation of these interfaces leads to an increase in the Electrical Contact Resistance (ECR) and, to some degree, a Thermal Contact Resistance (TCR) for the *p*-type leg at these interfaces. The TCR correlates with the decrease in open circuit voltage observed for the *p*-type legs over time and ECR correlates with the increase in internal resistance for the *p*- and *n*-type legs.

It is therefore necessary to quantify the ECR and TCR variations over time and temperature to best predict the degradation over time and, in turn, the predicted SKD-MMRTG power output over time. This is accomplished by both extracting the ECR and TCR values from couple life test data and developing extrapolation models based on couple DPA results and couple test data. The DPA results inform when the degradation associated with the chemical reaction at the hot-side interfaces will be completed and when the degradation will level off. The ECR and TCR model is being continuously refined as more DPA data is generated and more test data becomes available.

The current best SKD-MMRTG and MMRTG 17-year power output prediction estimate based on current ECR and TCR best estimates for *n*- and *p*-type legs is shown in Figure 10. The prediction assumes 3 years of storage followed by 14 years of operation. The predictions were made as a function of beginning-of-life fuel inventory (Q), generator fin root temperature (T_{fr}), and load voltage (V). The typical load voltage for MSL and M2020 MMRTGs is about 30V. The SKD-MMRTG could deliver at least 38% more power than the MMRTG at equivalent

conditions. This is a significant improvement that could enable substantially more science for a spacecraft/rover that would use an SKD-MMRTG compared to an MMRTG.

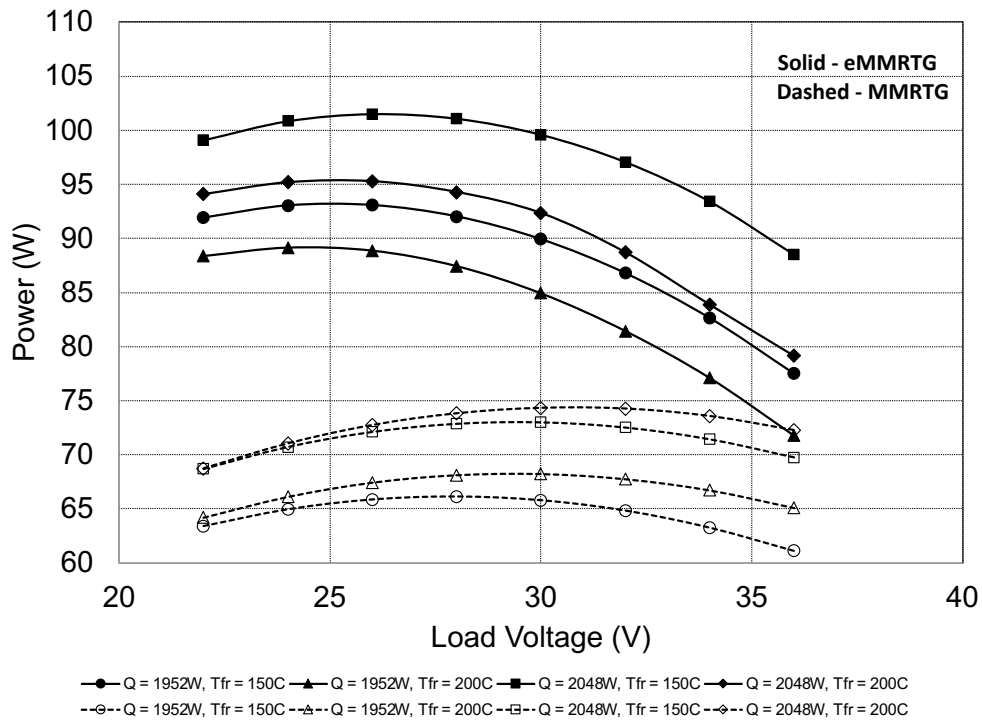


FIG 10. Comparison of current-best-estimate SKD-MMRTG and eMMRTG 17-year power output prediction as a function of beginning-of-life fuel inventory (Q), generator fin root temperature (T_{fr}), and load voltage (V). The prediction assumes 3 years of storage followed by 14 years of operation. The typical load voltage for MSL and M2020 MMRTGs is about 30V.

The second advanced RTG TE converter technology under development at JPL is illustrated in Figure 11. The cantilevered uncouples depicted in the figure would utilize the lower-temperature SKD segment materials demonstrated in the SKD-MMRTG couples segmented to high-temperature TE material segments made of $Yb_{14}MnSb_{11}$ and $LaTe_{1.45}$ (that is, $La_{3-x}Te_4$ with $x \sim 0.25$) for the *p*- and *n*-type material, respectively.^{55,56} It requires an inter-segment compliant layer to accommodate the coefficient of thermal expansion mismatch between the upper segments and the lower segments of the uncouple. The key challenge is to

develop stable (multi-years of operation) metallization interfaces between the upper TE materials and the heat collector at temperatures up to about 1000°C.

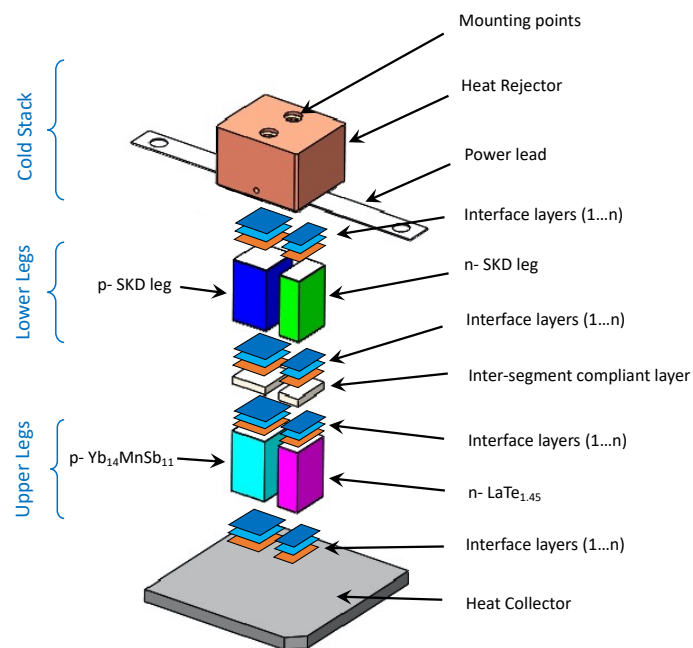


FIG 11. Illustration of the high-temperature, cantilevered unicouple under development at JPL.

While this technology is currently at a rather low technology readiness level, it potentially offers substantial increase in efficiency. Table 1 shows a comparison of the couple-level TE efficiencies for various RTG TE couple technologies. Considering the impressive and reliable performance track-record of RTG TE couple technologies that were used in the past or are in use and the very stringent requirements including decades of operation, validating new TE couple technologies require a thorough manufacturing and performance verification plan that typically requires multi-year program to execute. The $\text{Yb}_{14}\text{MnSb}_{11}/\text{LaTe}_{1.45}/\text{SKDs}$ unicouple technology is, in that respect, in its infancy but offers a formidable potential that deserves to be further assessed.

Table 1. Comparison of the couple-level TE efficiencies for various RTG TE couple technologies.

| Technology | TE efficiency (%) | T _{hot- junction} (°C) | T _{cold- junction} (°C) | Type of couple |
|---|-------------------|-------------------------------------|--------------------------------------|--------------------------|
| MMRTG (PbTe-TAGS) | ~ 7.5 | 525 | 210 | Spring-loaded, cover gas |
| GPHS-RTG (SiGe) | ~ 8.0 | 1000 | 300 | Cantilevered, vacuum |
| SKD-MMRTG | ~ 9.5 | 575 | 210 | Spring-loaded, cover gas |
| Yb ₁₄ MnSb ₁₁ /LaTe _{1.45} /SKDs | ~ 14.0 | 1000 | 300 | Cantilevered, vacuum |

IV. FUTURE RESEARCH DIRECTIONS

The last two decades have witnessed the emergence of novel families of compounds, with some of them demonstrating remarkable TE properties that outperform those of the state-of-the-art materials.^{1,7,8} These discoveries have been guided by the development of various strategies and the reinvestigation of known materials with modern techniques. However, many of them, for which outstanding results were reported, do not meet the requirements for being integrated in TE devices or RTGs due to thermal stability aspects even under inert atmosphere. For instance, compounds with mobile ions, although appealing due to their extremely low lattice thermal conductivity,^{57,58} rapidly degrade when subject to high current densities. Assessing the stability and ageing of novel compounds is thus of prime importance and should be more systematically performed under atmospheres close to those of applications.

Seeking for novel materials less sensitive to oxidation in the medium-to-high temperature range would be an interesting step toward mitigating the needs for protective layers, one of the

major material-specific issue that remains to be solved. Examples of such materials include β -FeSi₂ and to a lesser extent higher manganese silicides (HMS) MnSi _{γ} ($1.7 < \gamma < 1.8$).^{59,60} In this regard, the possibility to reduce the length of the TE legs leads to increased output power, thereby enabling to use lower temperature gradients. More systematic studies on known TE compounds would be welcome to determine the maximum temperature above which oxidation starts to degrade the material performance.

In addition, medium-temperature braze and efficient diffusion barriers require time-consuming trial-and-error experiments. Because most TE compounds show optimum TE performance at medium temperatures, identifying brazes specific to this temperature range is pivotal to avoid deteriorating the TE compounds during this fabrication step. The use of Ag nanoparticles has recently proved to be effective in reducing the reactive temperature while achieving excellent electrical and thermal contacts between the TE materials and the electrical connections.⁶¹ This possibility opens up new avenues to design novel brazes that might be used with various families of TE materials.

Despite the difficulties faced in protecting the TE materials against oxidizing atmospheres, more systematic studies devoted to these aspects would be important. One crucial aspect is that a good match between the thermal expansion coefficients of the TE materials and the protective layers should be achieved, which limits the candidate compounds that can be considered. Overcoming this issue by aerogels may be re-evaluated for specific applications where the available space and cost are not limiting factors.

In determining the thermal stability of TE materials and devices, only a small number of heating/cooling cycles are applied, resulting in a limited number of hours during which the thermal behavior of the materials and interfaces can be assessed. As evidenced by the two examples of RTG technologies discussed in the previous part, these studies should be performed over sufficiently long periods of time to better evaluate the lifetime of the TE devices and the

rate of power degradation. Although time-demanding, such studies are essential to fully qualify the fabrication process.

Should it be for industrial or space applications, conventional π architectures remain the preferred one due to its simplicity to be manufactured. In addition, the TE legs typically retain a parallelepiped shape while other, more complex shapes may offer advantages in terms of conversion performance.⁶² Additive manufacturing could be envisaged to realize complex shapes, paving the way for topological optimization. Moreover, this technique would offer the possibility to fabricate TE devices with non-planar top and bottom surfaces (tube trapping a moving fluid for instance), which would facilitate the coupling between the TE devices and the hot or cold source. Even though this technique has already been applied to TE materials,^{63,64} it implies novel challenges to be overcome. Firstly, this technique cannot be employed for TE materials under oxidizing atmosphere to avoid oxidation during the synthesis step. Secondly, the TE properties of the best materials are often highly sensitive to defect chemistry, the control of which may be extremely difficult to ensure experimentally with additive manufacturing. Thirdly, materials with optimized TE properties are typically heavily alloyed with a high number of elements that can exhibit high vapor pressure. Whether homogeneous materials can be obtained by this technique is another important issue that should be carefully studied.

Finally, another aspect to consider is the development of a smart electronic interface enabling to operate at the maximum operating point. This issue now seems to be well mastered under stationary conditions (such as in space for example) but needs more development when the temperature difference between the hot and cold source is time dependent (such as in automobile for example).

V. CONCLUSION AND FUTURE OUTLOOK

Converting heat into electricity remains the technology of choice for space missions. In RTGs, the length of the TE legs is typically on the order of 1 cm to minimize thermomechanical stresses undergone by the TE materials. With a finite amount of radioisotope fuel, the conversion efficiency and the output power per kg are the key parameters for space missions. The two technologies presented here will allow the development of the next-generation RTGs that will be used for the continuing exploration of the solar system in the coming decade. Over the last couple of years, significant efforts were also devoted to the development of TEGs integrating various novel, highly-efficient TE materials with the aim at optimizing either the conversion efficiency or maximum output power. With several families of materials successfully integrated into TEGs, this delicate, yet necessary critical step may keep pace with materials discovery in the near future. While most studies on TEGs have been devoted to maximizing the conversion efficiency, developing devices specifically designed to generate an optimized output power is also of particular interest for a broad range of applications. However, this requires shortening the length of the TE legs to values that can cross the threshold below which the mechanical stability of the legs can no longer be ensured. One possible solution discussed in this perspective to overcome this issue is the intercalation of metallic composites that act as mechanical buffers, maintaining the mechanical stability of the legs upon cycling. Beyond merely generating high output power under large temperature differences, this solution also offers the possibility to limit the temperature applied at the hot side while still maintaining the output power to a sufficiently high value to be of interest for various industrial applications. The protection of the TEGs against oxidation is the critical next step to undertake to bring these devices closer to applications. In this regard, the strategy of shortening the TE legs discussed above may help to mitigate this notoriously-difficult problem by limiting the hot side

temperature and hence, oxidation issues. Extending this strategy to other advanced TE materials, either mechanically robust or mechanically protected by metallic composites, may provide opportunities to develop novel power generation applications.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

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

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