

# **“Development of Functional Nanostructures for the Conversion of Thermal to Electrical Energy”**

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**A collaboration between Applied Innovation Alliance, West Bloomfield, MI**  
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## ABOUT THE AUTHORS

This paper is a collaboration between Dana W. Clarke, Sr. of Applied Innovation Alliance (AIA), and Dr. Gafur Zainiev of Fluid Insights. AIA is a consulting firm that specializes in Structured Innovation and intellectual property development. AIA will bring a unique approach to identifying and solving issues with known TEG technology. Past clients have spanned industries from automotive and defense contractors to research laboratories. Fluid Insights is a company specializing in the processing and analysis of extremely small quantities of fluids. Fluid Insights has developed inventive approaches to fluid analysis in medical diagnostics, as well as creating new solutions for optimizing fluidic reactions. Both companies boast teams of inventors, PhD level scientists, engineers and entrepreneurs.

## ABSTRACT

This paper provides an overview of known issues (contradictory or conflicting requirements) associated with Thermoelectric Generators (TEG's), how inventive and experimental approaches will be used to create more efficient TEG's and the development of an Industrial-Scale MicroReactor™. Also addressed are the high-speed automation of laboratory research and its smooth transition to production without scalability issues.

Specifically we will focus on how material properties and configuration will be manipulated and experimented with to gain higher TEG efficiency. Subsequently, we will discuss how design of experiments and artificial intelligence optimization methods will be incorporated to support high-throughput screening for the development and optimization of practical nano-level waste heat recovery sub-systems.

## INTRODUCTION

Why build TEGs? Research indicates that well over 8.4 million megawatts of energy is lost in waste heat globally. It is there for the taking, and today we have the ability to combine, integrate and hybridize existing technologies to capture a significant portion of it.

Current TEG efficiency is in the area of 5-15%(1). We believe that traditional laboratory processes are too slow and somewhat archaic. If the global average of thermal efficiency is 40% or less, the ability to recapture even 10-15% is truly a significant breakthrough but it is only scratching the surface.

Fabrication of functional nanostructured materials for the development of thermal-to-electric generators (TEG) requires practical approaches for self-assembly of nanoparticles in unique compositional and geometric configurations with smooth transition from the lab to production. Synthesis of nanoparticles is the beginning; subsequent steps require development of nanoparticle building blocks arranged in distinct assemblies and super-structures that will lead to the ability to fully leverage novel / unique properties observed in the lab for practical application in the field.

It is believed that the development of practical nanocomposite TEG coatings and structures formed of complex combinations of different types of organic and/or inorganic nanoparticles with 1nm-300nm diameters will be required to effectively and efficiently convert thermal energy to usable electrical energy.

To achieve this globally important objective, we are targeting one of the most promising strategies for fabrication of such hierarchical structures, the use of self-assembly processes coupled with the real need for high-throughput screening (HTS) in the lab and the immediate transition to production. The arrangement of such structures will be

ascertained by interactions among the primary building blocks (materials and configurations) and adequately tailored surface properties (the fundamental parameter in the design of novel nanobuilding blocks).

Currently under development is an Industrial-Scale MicroReactor™ capable of delivering HTS of materials, conditions, characteristics, configurations and regimes for creating nanostructures on any surface to produce the desired thermal-to-electric characteristics. The Industrial-Scale MicroReactor™ will equate to a hyper-version of Edison's time consuming approach to the identification of an improved filament for the incandescent lamp. While Edison painstakingly conducted thousands of trial and error attempts over years, our plan will deliver and evaluate thousands of combinations per week through fully automated, computer controlled "designed and full-factorial" experimentation applied to combinatorial chemistry / nanoparticle process that supports self-assembly and immediate measurement.

## A PROCESS FOR EXPERIMENTATION

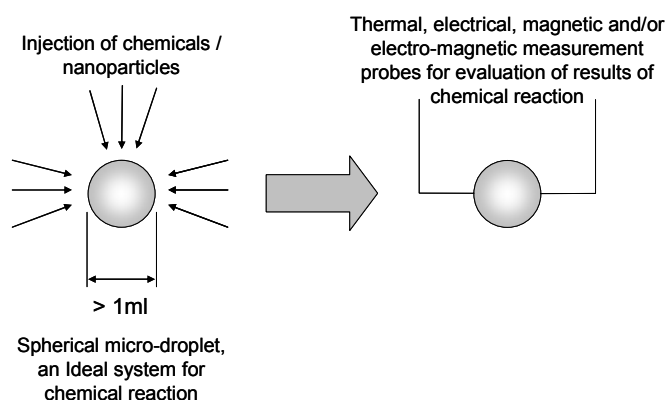
Today, TEG technology is severely limited by the efficiency of its components and their assembly. To adequately improve the efficiency of TEG technology systemically, the limits of its component efficiency must be comprehensively understood through in-depth experimentation and analysis.

The process associated with the Industrial-Scale MicroReactor™ will provide a temperature and pressure controlled environment for conducting combinatorial chemistry and the self-assembly of nanoparticles experimentation in micro-droplets of less than 1 ml volume (Fig. 1) versus the extremely high-cost, low-productivity approaches of chemical vapor deposition or plasma vapor deposition.

The key innovations associated with the Industrial-Scale MicroReactor™ are that it resolves the contradictions associated the

optimization of chemical reactions, the formation of nanoparticle composite coatings / structures on various material surfaces and immediate

evaluation (measurement) of the results. The Industrial-Scale MicroReactor™ will be capable of combining a multitude of different chemistries and nanoparticles in different volumes plus measure and report the results to a computer for analysis, modification of next stage designed experiments and data storage.



Ideal System  
Fig. 1

## MATERIALS RESEARCH

The efficiency of a TEG is based heavily on the efficiency of the material used for the bridging of hot-to-cool zones (1). Efficiency of a Seebeck material, however, is a contradiction\*; materials must be of both high electrical conductivity while at the same time having limited electrical conductivity (2).

\* While we are only addressing one contradiction in this paper, there are, in fact, numerous contradictions associated with TEGs that must be resolved through innovation and experimentation. These contradictions exist in two basic forms: 1) complex: as one characteristic is improve – another degrades; 2) simple: a characteristic must be in opposite states.

Elements and compounds that have favorable Seebeck efficiency are known today (3), but they still have issues and are far from ideal. In order to breakthrough to the next level of TEG efficiency, we must first understand what the limiting factors are in material efficiency and next resolve the contradictory requirements, for example, high conductivity and low conductivity can often be resolved by separation principles, for example: separation in time (high at one point in time and low at another point in time); separation in space (high in one location and low in another); separation upon changing conditions (high under one condition and low under another condition); and/or

separation between the way parts of the system are vs. the whole system (high for one element in the system and low for the overall system).

Traditionally, research on thermoelectric materials has focused on discovering or combining materials that have the proper balance of the relevant properties (4). While this approach has yet to yield breakthrough results, our process is expected to significantly enhance this endeavor. By utilizing designed and/or full factorial experiments for combinatorial chemistry of a multitude of chemicals and nanoparticles at extremely high experimentation rates, a larger number of possibilities will be visible. Likewise, by controlling the micro-droplet size for optimum reactivity, results will be fast and of high quality.

Beyond combining chemistries and nanoparticles, we will study individual materials themselves. One such approach is to examine a material's thermoelectric figure of merit. For efficient energy conversion, this number needs to remain high but the figure of merit has approached its limit for bulk materials (5). This is tied to the contradiction of needing high and low electrical conductivity. Two known approaches plus other to be conceived approaches will be taken to address this issue.

$$ZT = [(S^2\sigma)/\kappa]T$$

ZT = Figure of Merit; S = Seebeck Coefficient;  $\sigma$  Electrical Conductivity;  $\kappa$  = Thermal Conductivity; T = Temperature

Approach A: Although bulk materials may have reached the limit of thermoelectric efficiency, nano-materials have not. Studies show that nanowires are capable of a higher thermoelectric efficiency than their bulk material counterparts (6). This is due in part to quantum confinement effects and increased phonon boundary scattering (7). Likewise, a change in the shape of the energy density of nanowires compared to bulk materials allows for the increase of the Seebeck coefficient, thus increasing the overall thermoelectric efficiency.

Example: In Bismuth, an element commonly used in TEG applications. The bulk form semi-metal Bismuth has a very low Seebeck coefficient. When, at the size of formed nanowires, however, Bismuth forms sub-bands in the direction where quantum confinement occurs (8). This may allow for Bismuth nanowires to be used as an effective material for TEG applications.

Approach B: An alternative is to manipulate electron filtering and phonon scattering thus increasing thermoelectric efficiency through the introduction of nano-particles. By introducing nano-particles into existing compounds or structures, the functionality of added charge carriers can be incorporated, thus decreasing thermal conductivity.

Example: This approach is the introduction of ErAs nano-particles into a InGaAlAs structure. By taking a material that had been theoretically shown to effectively scatter phonons and serve as both an electron filter and charge carrier (ErAs), the thermal conductivity of InGaAlAs was able to be significantly reduced (9). This approach was seen to significantly boost the amount of power output by a TEG system.

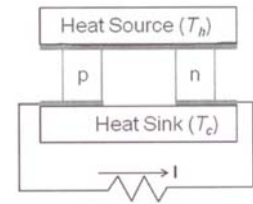
These approaches, however, need further exploration. Nanowires, other nano-structures and nano-particles can have their size, shape and configuration optimized, as well as in-depth experimentation on how each of those affects specific element or material choices. These approaches will all be enhanced by high-throughput screening in the Industrial-Scale MicroReactor™ to deliver dramatic new results.

## CONFIGURATION INNOVATION

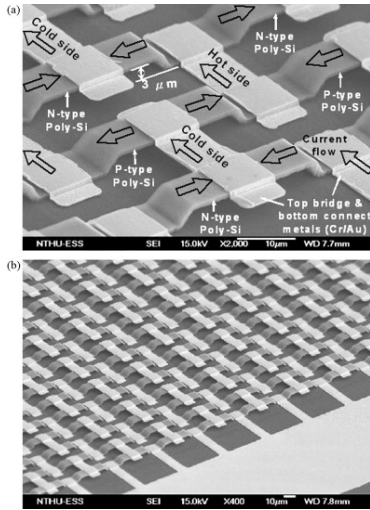
TEG technology is not merely a study of materials and material combinations. In order to properly optimize a TEG device and its output, a solution that incorporates an optimized configuration must be considered. This will be attacked by looking at three main elements: 1) the configuration of individual thermoelectric elements; 2) the systemic configuration of multiple thermoelectric elements; and 3) the configuration and opportunity associated with macro-scale connectors, nano- or micro-scale heat pipes, or other technologies that may be needed to fully functionalize and optimize TEGs.

A single thermoelectric element can be represented by the schematic drawing in Fig. 2 (10). We've already discussed how manipulating the materials in such an element may increase efficiency of a TEG, but what about

the configuration of the element itself? How can the geometry and distances between the components of the pictured element be manipulated for optimal performance? Does what we know about these geometries and distances change as we transition towards nano-level structures? Likewise, what are the thicknesses and densities of each component? What are the temperatures and heat densities in the heat source and sink? Much remains to be learned about optimum TEG configurations, especially as we transition these elements to smaller scale structures and speed of experimentation is the key.



Single Thermoelectric Element Fig. 2



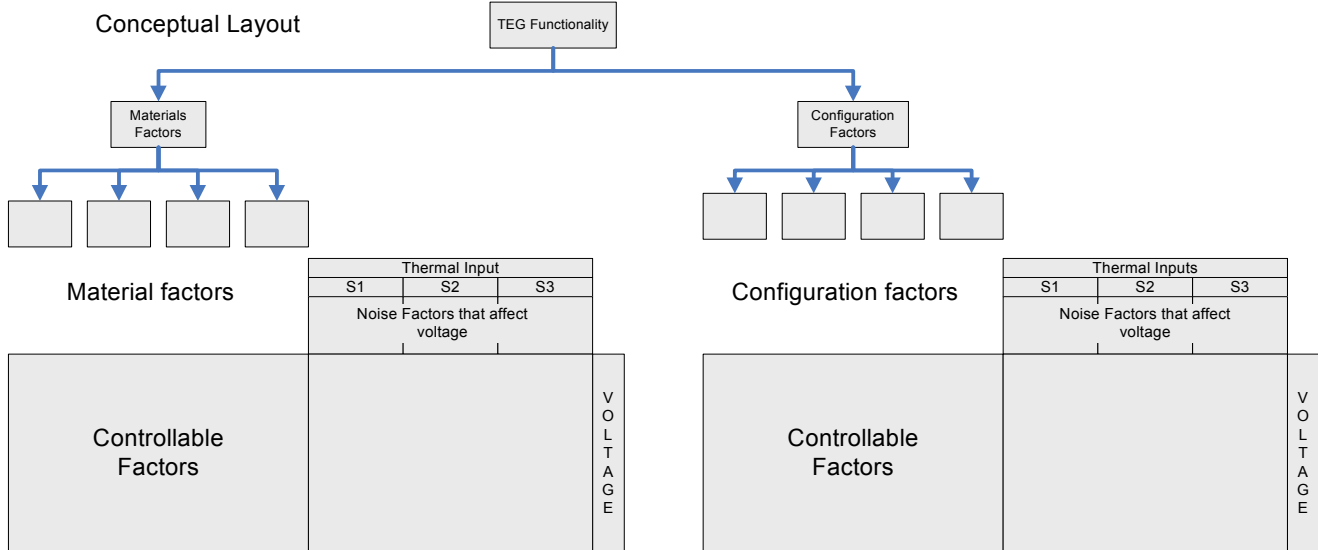
Woven Structure Fig. 3

Perhaps more interesting are the possibilities to be explored at the systemic level. A single thermoelectric element does not make a complete TEG system. There needs to be a combination of elements to obtain meaningful power from a system, which begs the question, what does a combination of thermoelectric elements look like? One example, of a woven structure, is pictured in Fig. 3 (7). But what other possibilities are there? How is the system wide configuration of thermoelectric elements optimized for efficiency? Are woven mats of elements the answer? Or longer, wire-like structures? These variables also need to be explored as we move from bulk material to nano-level constructions.

Lastly, an understanding of additional components needs to be developed. For example, if the heat sink in the thermoelectric element requires cooling, how should that function be delivered? Some suggestions point to the use of costly, energy consuming fans for air circulation processes, others to fins like in microprocessors. Still others advocate the use of heat pipes. Also, as we are transitioning this technology to the nano-level, we must remember that we are still applying it to macro interfaces. This means we must understand how to properly and efficiently transition our small scale structures to large scale connections.

## DESIGN OF EXPERIMENTS, GENETIC ALGORITHMS AND OPTIMIZATION

As made evident throughout the body of this paper, there are many ways to manipulate the efficiency of TEG systems; materials, substrates, particle sizes, structures and configurations. Each will drive the need for designed experiments and localized optimization (Fig. 4) plus the overall optimization as one integral system. Designed experiments provide systematic ways to deal with complex sets of variables, effectively gleaning useful results.



Designed Experiments / Localized Optimization Fig. 4

Why DOEs? Imagine selecting 27 types of nano-particles from the periodic table plus having a desire to experiment with each of three different sizes of particles between 1 nm and 300 nm. What is the total number of combinations that you would have to experiment with?  $3^{27}$  or roughly 7.6 trillion combinations or in simple terms, far too many to do manually on a trial and error basis. The utilization of orthogonal arrays in designed experiments can reduce the number of experiments to 27 experiments with an output that yields a prediction of the best combination of the 7.6 trillion possible combinations. This prediction is followed by a confirmation run that validates the prediction. But this only helps define the direction, i.e., element one at size 1, element 2 at size 3, element 3 at size 1 and so on – but remember, we had hundreds of possible sizes so we need to conduct a second, third and more experiments to zero in on the best combination.

Why automate the DOE process? Now imagine being able to run one experimental trial every 30 seconds, i.e., combining the appropriate chemistries / nanoparticles and measuring the results. For comprehensive results we will need to add testing at three different input temperatures and repeat each experiment 10 times for each of the 27 experiments discussed above for a total of 24,300 seconds. Add the ability to continuously run experiments 24/7 (or 604,800 seconds/week) with automatically reconfigured experiments 24 times a week with each subsequent experiment zeroing in closer and closer to the optimum.

Combine this discussion with the need to identify not only the best possible elements and compounds; sizes, shapes and geometries plus configurations and it is easy to see why the automation of experimentation within the Industrial-Scale MicroReactor will be of such high value.

Going beyond these simple examples, the principals of Applied Innovation Alliance have developed a proprietary process that combines evolutionary programming using Genetic Algorithms with DOEs. This process not only delivers optimization through traditional design of experiments but allow for optimum selection of factor levels to drive dimensional and process variability, beyond traditional DOEs, toward zero thereby significantly reducing the impact of tolerances.

Genetic Algorithms can also standalone to provide a means of creating equations from empirical data where no equations exist and can be used to optimize equation variables and tolerances where equations do exist.

Initial inputs to this process and methodology are a set of known equations and previously identified materials and configurations. These equations, however, are only a starting point for what we will learn through this process. It is necessary to understand and have in place methods of evolving known equations and documenting and developing new equations from raw data. By combining our continuously evolving results and raw data from the DOE's with known values, a Structured Innovation technique called Resource Profiling which is used to identify missing equation variables and equations from today, we can both build new equations from raw data, as well as evolve known equations. This affords us the opportunity to evolve our knowledge as breakthroughs are achieved, allowing for the quick leveraging of new knowledge.

## CONCLUSION

Waste heat is a tremendous resource in the world today. There is amazing potential to tap into a massive amount of waste energy readily and freely available. Existing technology, however, has only produced marginally practical TEGs having efficiencies in the single digits with research going only slightly farther. To make this technology viable, we need a comprehensive approach to managing the optimization of all controllable aspects of thermoelectric devices. This includes materials and chemistries, nano-structures, configurations and the methodologies needed to test all possible combinations. An approach that considers these factors can be successful in evolving TEG technology to a viable level of efficiency.

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