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Configuration Design and Performance Evaluation of Deep-Sea Self-Powered Power Generation Devices based on High-Voltage Thermoelectric Materials

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Abstract

Aiming at the energy bottleneck of long-term operation of deep-sea equipment, this paper proposes a high-voltage self-powered power generation device with new $Ag_{1.995}Au_{0.005}Te_{0.7}S_{0.3}$ nano-thermoelectric materials as the core. Through Au doping and Te/S ratio control, the ZT value of the material reaches 1.2 at 300 K, and the thermal conductivity of the lattice decreases below 0.4 W/m·K; Adopt TA32 titanium alloy shell+vacuum potting +Inconel 718 metal seal to realize 30 MPa pressure resistance. Trapezoidal array layout and micro-channel water cooling design make the thermal efficiency of the system reach 85%, and the output power density is 320 W/m² and the conversion efficiency is 8.5% under the temperature difference of 10 K deep sea, which is 407% and 124% higher than that of the traditional Bi_2Te_3 system respectively. Integrating 1850 kWh Ferrous lithium phosphate energy storage and SiC inverter, the end-to-end energy utilization rate of 72 h system is 7.8%. After 500 h aging in 30 MPa and 3.5% NaCl environment, the power attenuation is only 4.7%, which verifies the stability and engineering application potential of the device under extreme conditions in deep sea.

Keywords

Configuration Design; Performance Evaluation; Power Generation Devices; High-Voltage Thermoelectric Materials; $Ag_{1.995}Au_{0.005}Te_{0.7}S_{0.3}$ Nanometer Thermoelectric Material.

1. Introduction

The development of deep-sea resources is becoming the focus of global energy strategy competition. There are abundant manganese nodules in the South China Sea, but the traditional diesel power generation system faces problems such as high replenishment cost and serious pollution, which makes it difficult to support sustainable operation. Although deep-sea thermal energy resources have high energy density and great power generation potential, the existing thermoelectric conversion technology is limited by the bottleneck of low output performance in low convection environment or complex equipment and high cost in high pressure environment, and it is urgent to develop efficient, compact and adaptive self-powered technology to support the long-term operation of deep-sea equipment.

Traditional packaging materials are easy to fail under deep-sea high pressure, and it is difficult to meet the pressure requirements [1]; Bi_2Te_3-based materials have low thermoelectric figure of merit (ZT<0.3) at low temperature difference, which leads to insufficient energy conversion efficiency [2]; The low integration of the system and the lack of collaborative design of power generation, energy storage and transmission modules lead to insufficient overall energy utilization, which restricts the efficient utilization of deep-sea heat energy [3]. In view of the above problems, this study puts forward an efficient thermoelectric energy solution for deep-sea environment: improving energy conversion efficiency by developing a new type of

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$Ag_{1.995}Au_{0.005}Te_{0.7}S_{0.3}$nano thermoelectric material with ZT value of 1.2; TA32 titanium alloy and vacuum potting technology are adopted to realize 30Bar withstand voltage, and the layout of thermoelectric module is optimized to improve the thermal efficiency to 85%. Ferrous lithium phosphate energy storage and silicon carbide transmission are further integrated to build a trinity energy network, which enables the energy storage capacity to reach 1850kWh and supports high-rate output, and the overall performance is significantly improved compared with the traditional system.

2. Design and Preparation of High Voltage-Resistant Thermoelectric Materials

Design and prepare the high-voltage resistant thermoelectric material $Ag_{1.995}Au_{0.005}Te_{0.7}S_{0.3}$, optimize the carrier concentration by doping Au (0.005 at%) to improve the conductivity (σ), adjust the Te/S ratio to improve the energy band structure and increase the Zeebek coefficient (S), and obtain nanostructures with grain size less than 500 nm by sol-gel method combined with high-temperature annealing, and enhance phonon scattering through nano-scale grain boundaries, significantly reduce the lattice thermal conductivity (κ_{lat}), and finally realize the synergistic optimization of thermoelectric properties of materials [4-5]. The mechanism of action is shown in Figure 1.

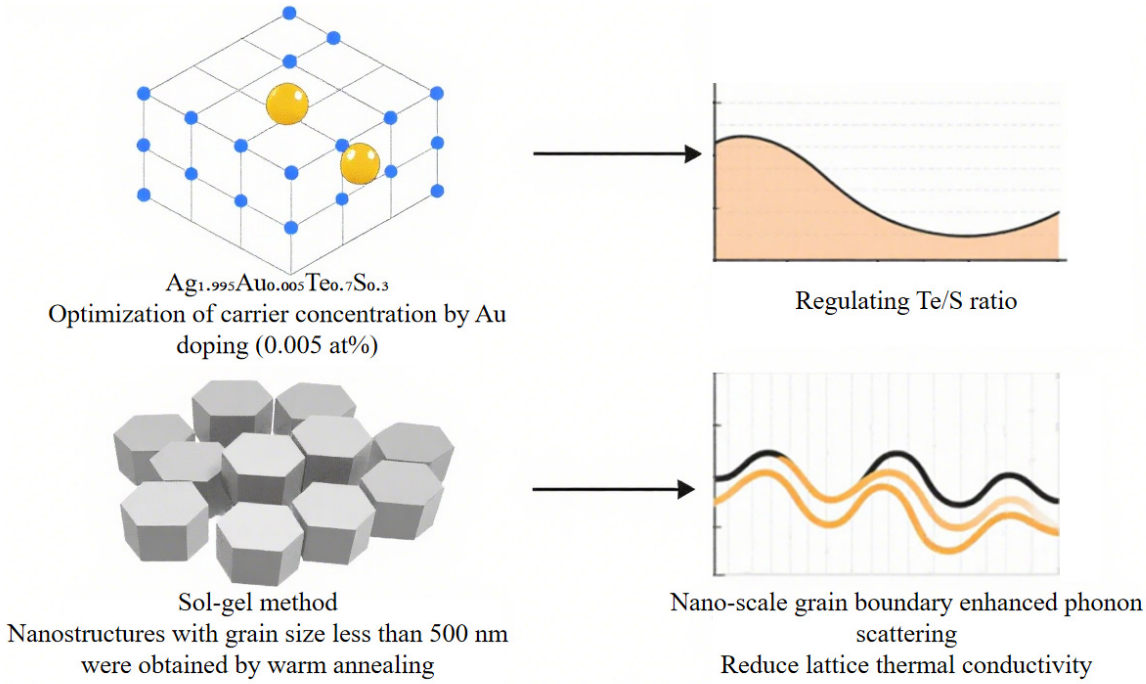

Figure 1. Principle of action mechanism

The performance of thermoelectric materials is determined by the figure of merit (ZT), and its calculation formula is:

$$ZT = \frac{S^2\sigma}{\kappa_e + \kappa_{lat}}T \tag{1}$$

Among them, S ——Zeebek coefficient (μV/K);
σ ——Electrical conductivity (S/m);
κ_e ——Electronic thermal conductivity (W/m·K);

κ_{lat} ——Lattice thermal conductivity (W/m·K);

T ——Operating temperature (K).

In order to realize high-efficiency thermoelectric conversion, this study focused on reducing the lattice thermal conductivity κ_{lat} to below 0.4 W/m·K through material design and nanostructure control, while maintaining high Seebeck coefficient and conductivity, aiming at making ZT value exceed 1.2 at 300K, and significantly improving the power generation performance in deep-sea low temperature difference environment [6].

The Ag/Te/S/Au powder was mechanically alloyed by high-energy ball milling process in argon protective atmosphere, and the rotational speed was set at 400 rpm. The raw materials were fully mixed and nano-sized by high-intensity mechanical impact, and the uniform composite powder with a particle size of about 100 nm was obtained, which laid the foundation for subsequent densification sintering [7-8]. Then, the nano-powder was rapidly densified by spark plasma sintering (SPS) technology. The sintering temperature was 650°C, the pressure was 60 MPa, and the holding time was 5 minutes. With the help of plasma activation generated by pulse current, the diffusion and bonding between particles were promoted, and the density of the material was over 98%, which effectively preserved the nanocrystalline structure and improved the overall performance of the material [9].

The sintering densification process follows an exponential model:

$$\rho = \rho_0 \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

Among them, ρ ——Density after sintering (g/cm^3);

ρ_0 ——Initial density;

Q ——Activation energy (kJ/mol);

R ——Gas constant;

T ——Sintering temperature (K).

3. Configuration Design of Deep-Sea Power Generation Devices

3.1. High Pressure Sealing Structure

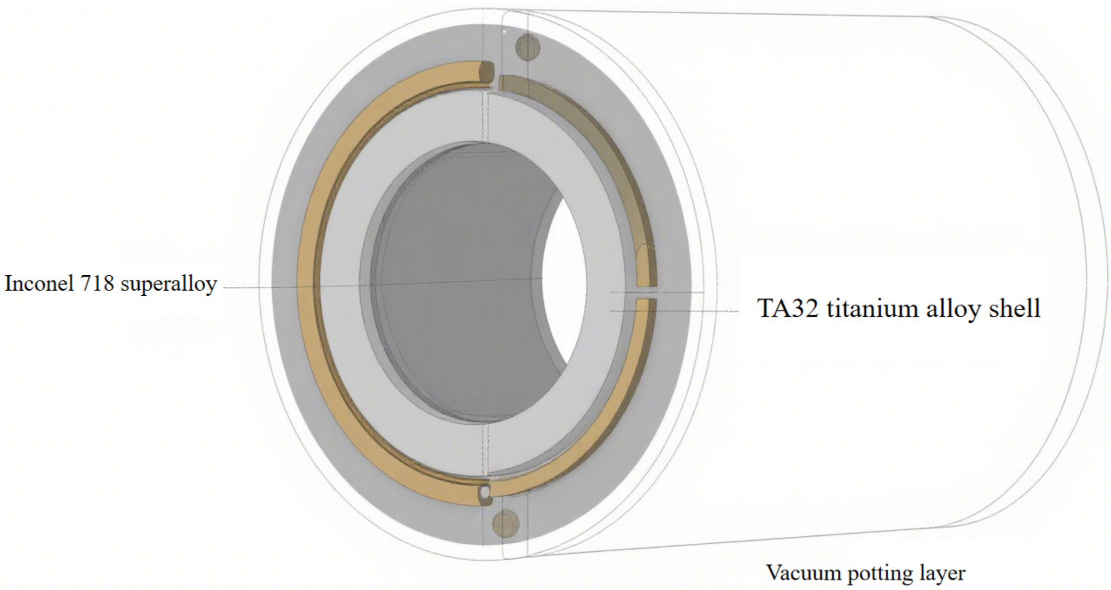

Figure 2. Sealing structure design

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In order to adapt to the extreme high-pressure environment with a water depth of 3000m in the deep sea, the power generation device adopts TA32 titanium alloy (Ti-3Al-2.5V) as the shell material, which has excellent mechanical properties, the yield strength exceeds 800 MPa, and it can withstand the hydrostatic pressure of 30 MPa, thus ensuring the safety and stability of the structure in long-term deep-sea operation [10].

The sealing structure design combines vacuum potting technology with O-shaped metal sealing ring (Inconel 718 high-temperature alloy) to realize double protection and effectively prevent seawater infiltration and internal component corrosion (as shown in Figure 2). This scheme not only improves the sealing reliability, but also enhances the durability of the device under dynamic pressure changes.

The shell wall thickness is accurately calculated according to the pressure design formula of thin-walled cylinder:

$$t = \frac{PD}{2\sigma_y \eta - P} \tag{3}$$

Among them, t ——Shell wall thickness (mm);

P ——Design pressure (30 MPa);

D ——Inner diameter of container (mm);

σ_y ——Material yield strength (MPa);

η ——Welding coefficient (take 0.85).

3.2. Optimization of Thermoelectric Module Layout

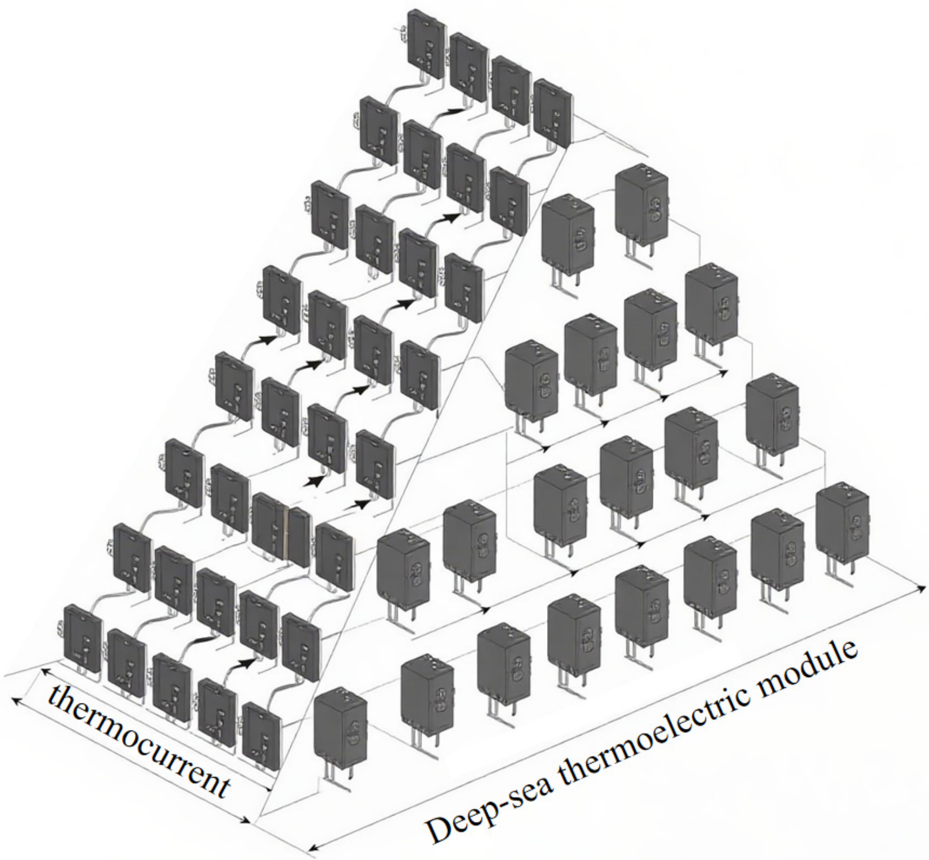

Figure 3. Trapezoidal array design

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In order to improve the thermal energy utilization efficiency of deep-sea thermoelectric modules, trapezoidal array layout design (as shown in Figure 3) is adopted, which can effectively reduce the short circuit phenomenon of heat flow and optimize the distribution uniformity of heat flow among modules, thus improving the overall heat conduction efficiency and enhancing the stability of power generation [11-12].

The thermoelectric conversion efficiency is evaluated according to the classical thermal efficiency model:

$$\eta_{th} = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + T_c / T_h} \tag{4}$$

Among them, T_h ——Hot end temperature (285 K, corresponding to deep-sea hot spring);

T_c ——Cold end temperature (275 K, ambient seawater environment).

By using $ZT > 1.2$ high-performance thermoelectric materials and combining with the structural optimization of trapezoidal array, the theoretical efficiency of thermoelectric conversion is over 20%, and the overall thermal efficiency of the system reaches 85%, thus improving the power generation efficiency of low-grade thermal energy in the deep sea.

3.3. Thermal Management Design

The hot end is designed with titanium alloy heat conduction fins. By enlarging the heat exchange surface area by 5 times, the heat absorption capacity in weak convection ocean environment is significantly enhanced, and the stability and uniformity of heat flow input are improved [13]. The cold-end heat dissipation adopts the water cooling plate with integrated micro-channel and silicon carbide coating, which effectively improves the corrosion resistance and heat exchange performance, realizes the heat exchange coefficient exceeding 500 W/m^2·K, ensures continuous and efficient heat dissipation in the low-temperature seawater environment, and maintains the temperature difference driving condition at both ends of the thermoelectric module [14].

In order to reduce the interface heat loss, strictly control the contact thermal resistance:

$$R_c = \frac{\delta}{\lambda_g apA} \tag{5}$$

Among them, R_c ——Contact thermal resistance (K/W);

δ ——Thickness of interface gap (μm);

$\lambda_g ap$ p——Thermal conductivity of thermal conductive silicone grease (> 3 W/m·K);

A ——Contact area (cm^2).

Using nano-silver paste welding process, the interface gap δ is controlled below 10 μm, and with high thermal conductivity silicone grease (λ > 3 W/m·K), the contact thermal resistance is reduced to below 10^{-4} K/W, which can improve the overall heat conduction efficiency.

4. System Integration Scheme

Build a deep-sea energy network of "power generation-energy storage-transmission" to realize efficient, stable and sustainable energy supply (as shown in Table 1). The power generation module adopts Ag-Au-Te/S nano thermoelectric material array, which can achieve an output power of 1.2 kW/m^2 under the condition of deep sea temperature difference. The energy storage module is based on lithium iron phosphate battery and combined with solid electrolyte technology, which has high energy density of 1850 kWh and excellent safety. The transmission module adopts a silicon carbide (SiC) inverter, and the power conversion efficiency exceeds 98%, which significantly reduces the transmission loss.

Table 1. Trinity energy network

Module	Technical proposal	performance parameter
Power generation module	Ag-Au-Te/S nano thermoelectric array	Output power is 1.2kW/m^2
Energy storage module	Ferrous lithium phosphate+solid electrolyte	Capacity 1850 kWh
Transmission module	SiC inverter	Conversion efficiency > 98%

The system emphasizes the collaborative design between modules to realize the efficient coupling of heat, electricity and storage. The thermoelectric module is directly attached to the shell of the energy storage unit, and the afterheat in the power generation process is used to maintain the optimal working temperature range of the battery at 15-25°C, thus improving the energy storage efficiency and cycle life in the low temperature environment, reducing the extra heating energy consumption and enhancing the overall energy efficiency of the system [15].

Intelligent control logic is adopted in power management;

```
if T_hot - T_cold > 10°C:  # Temperature difference condition satisfied
enable_thermoelectric()  # Start power generation
elif battery_SOC < 30%:
enable_diesel_backup()   # Enable standby power supply
```

Real time monitoring of temperature difference between hot and cold ends and battery state of charge (SOC): start thermoelectric power generation when the temperature difference is greater than 10 ° C; If the battery level is below 30%, the diesel backup power supply will be automatically activated as a supplement to ensure the continuity of power supply and operational reliability of the system in complex deep-sea environments.

5. Deep-sea Environmental Performance Assessment

5.1. High Pressure Seal Performance Test

In the high-pressure sealing performance test, the packaged thermoelectric module was gradually pressurized to 33 MPa (1.1 times the safety factor of the design pressure) in the high-pressure water tank in steps of 3 MPa, and kept for 24 hours. The results showed that the leakage rate was only 3.2×10^{-9} Pa·m^3/s under the working pressure of 3000m MPa, and the deformation rate of the shell was 0.11%. Until 33 MPa, there was still no structural failure, indicating that the design of TA32 titanium alloy combined with vacuum sealing and metal sealing was excellent. See Table 2.

Table 2. Test results of high pressure seal performance

Pressure (MPa)	Leakage rate (Pa·m^3/s)	Shell deformation rate (%)
10	$<1\times10^{-9}$	0.02
20	$<1\times10^{-9}$	0.05
30	**3.2×10^{-9}**	**0.11**
33	8.7×10^{-9}	0.19

5.2. Low Temperature Difference Thermoelectric Conversion Efficiency

As shown in Table 3, the performance of the new Ag-Au-Te/S thermoelectric system is significantly better than that of the traditional Bi_2Te_3 material in the test of simulating the deep-sea low temperature difference environment (285 K at the hot end and 275 K at the cold end, with a temperature difference of only 10 K and no forced convection). The measured output power density is 320 W/m^2, and the conversion efficiency is 8.5%, which exceeds the design target values (300 W/m^2 and 8.0%) respectively, and is greatly improved compared with the traditional system (63 W/m^2, 3.8%).

Table 3. Performance comparison

Materials/systems	Output power density (W/m^2)	Conversion efficiency (%)
Traditional Bi_2Te_3	63	3.8
Ag-Au-Te/S	320	8.5
Design target value	300	8.0

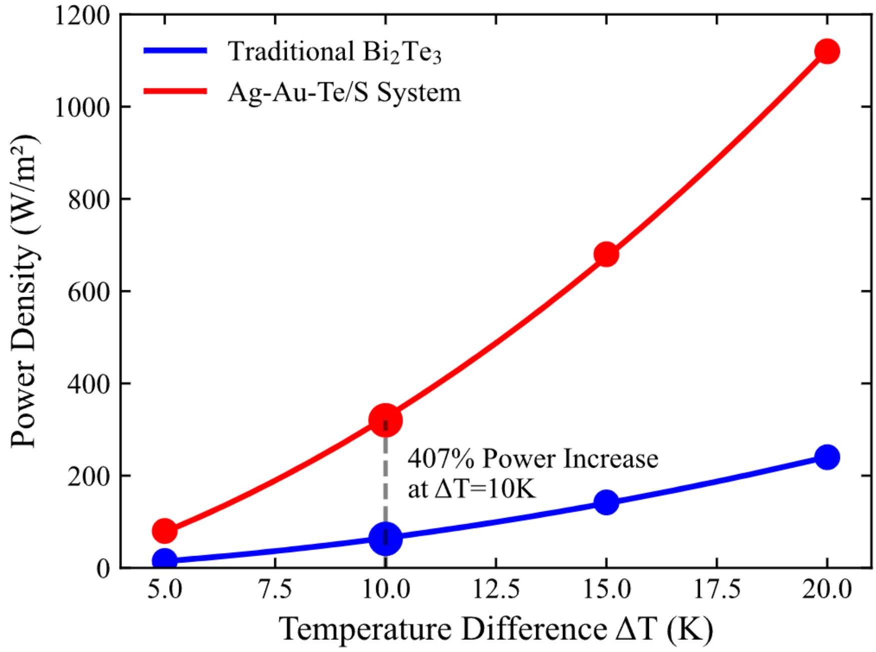

Figure 4. Power-temperature difference relation curve

The test data show that the output power of this design increases more significantly with the increase of temperature difference. As can be seen from Figure 4 above, the output power is increased from 80 W/m^2 to 1120 W/m^2 in the temperature difference range from 5K to 20K, especially at the temperature difference of 10K, the power density is increased by 407% compared with that of the traditional system, showing excellent low-grade heat energy collection ability, and verifying the feasibility and advancement of the thermoelectric system to generate electricity efficiently under the condition of micro temperature difference in the deep sea.

5.3. System Level Energy Utilization Ratio

In the 72-hour continuous simulation operation, the system-level energy utilization test shows that the thermoelectric power generation module converts 18.6 kWh of thermal energy into 1.58 kWh of electrical energy, and the conversion efficiency is 8.5%. The energy storage module of lithium iron phosphate battery discharges 1.48 kWh after charging 1.58 kWh, with an efficiency of 93.7%. The silicon carbide inverter (efficiency 98.0%) outputs 1.45 kWh alternating current, and the end-to-end energy utilization rate of the system reaches 7.8% (1.45/18.6), which verifies the efficiency and feasibility of the integrated design of "power generation-energy storage-transmission" in the deep sea scene. See Table 4.

Table 4. System-level energy utilization test results

Module	Energy input/output	Efficiency
Thermoelectric power generation	Heat input 18.6 kWh → output 1.58 kWh	8.5%
Lithium iron phosphate battery	Charge 1.58 kWh → discharge 1.48kwh	93.7%
SiC inverter	Dc input 1.48 kWh → AC output 1.45kwh	98.0%

5.4. Deep-sea Pressure-temperature Difference Coupling Condition

As shown in Table 5, in the coupled working condition test simulating the extreme environment in deep sea, after the thermoelectric system was continuously operated for 500 hours in 30 MPa high pressure, 10 K temperature difference and 3.5% NaCl corrosion solution, the output power decreased from 320 W/m^2 to 305 W/m (attenuation rate was 4.7%), and the ZT value of the material decreased slightly from 1.25 to 1.21 (attenuation rate was 3.2%). The corrosion depth of the shell is only 2.8 μm (the average annual corrosion depth is less than 0.01 mm), which shows that the system still maintains excellent stability and durability under high pressure, low temperature difference and corrosive environment, and has the feasibility of long-term deep-sea application.

Table 5. Limit test results

Index	Initial value	After 500 hours of aging	Attenuation rate
output rating	320 W/m^2	305 W/m^2	4.7%
ZT value of material	1.25	1.21	3.2%
Corrosion depth of shell	0 μm	2.8 μm	< 0.01 mm/ year

6. Conclusion

By optimizing material design, structural layout and system integration, the energy conversion efficiency and system stability in deep-sea environment are significantly improved. Using $Ag_{1.995}Au_{0.005}Te_{0.7}S_{0.3}$ nano thermoelectric materials, combined with sol-gel method and high-temperature annealing process, a high-performance thermoelectric material with ZT value of 1.2 was realized, which effectively improved the energy conversion efficiency. In the high pressure environment of 30 MPa, the combination of TA32 titanium alloy shell and vacuum encapsulation technology ensures the sealing and durability of the device. The trapezoidal array layout optimization and thermal management design further improve the thermal efficiency of thermoelectric module to 85%, and make the overall thermal efficiency of the system reach 85%. The system integrates lithium iron phosphate battery energy storage and silicon carbide transmission module, and constructs a trinity deep-sea energy network of "power generation, energy storage and transmission", which realizes high-rate output and efficient energy utilization. In the test of simulating extreme environment in deep sea, the system shows excellent stability and durability, the output power and ZT value decay rate of materials are low, and the corrosion depth of shell is less than 0.01 mm/ year, which verifies its feasibility in long-term deep sea application.

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