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Study of Solar Thermal Power Generation Based on Reverse Electrodialysis

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Abstract: TPG-RED (Thermal Power Generation Based on Reverse Electrodialysis) was studied to explore the new method of solar thermal power generating based on Reverse Electrodialysis (RED) in this paper. RED is a process that transfers the salinity gradient between sea water and fresh water to electricity. TPG-RED has combined RED with thermal power generation to transfer thermal energy from solar to electricity which has many advantages of huge available temperature range, sustainability, non-pollution, simple structure, and so on. Respectively, using "1 mol/L H_2SO_4 solution—0.0001 mol/L H_2SO_4 solution" and "1 mol/L Na_2SO_4 solution—0.0001 mol/L Na_2SO_4 solution" as the working medium at 30°C heat source temperature to carry out power generating experiment. After 400 min, both open circuit voltages reached 28.4 and 31.0 mV respectively and initial output current were 267 and 295 μA respectively, after 120 min discharging, the output current was basically stable, reached 7 and 5 μA respectively. The effect of heat source temperature on output current shows that TPG-RED can generate electricity at 20°C–55°C heat source temperature, and the output current increased with the temperature increasing. In the ion exchange membrane solution concentration limit, the output current increased with the concentration difference increasing.

Keywords: Solar energy; reverse electrodialysis; thermal power generation; temperature; concentration difference

1 Introduction

China's energy consumption is still dominated by fossil energy, which is mostly utilized in the form of thermal energy. Abundant thermal form of energy such as solar thermal and geothermal are stored in the natural world. In recent years, the solar energy as a kind of clean and renewable energy is applied in many areas [1,2]. With the increasing demand of energy conversion and waste-heat utilization, it is important to study how to use solar energy effectively [3,4].

Converting solar energy into electrical energy is one of the most valuable way to utilize solar energy [5]. At present, Solar thermal power plants can produce high-temperature heat that is converted into electricity by conventional power cycles [6,7]. The utilization of high-temperature thermal energy has been relatively mature, but for low-temperature thermal energy, it is still in the research stage.

Some thermodynamic cycles, such as the Organic Rankine Cycle (ORC) and the Kalina Cycle are applied to industrial waste heat power generation. ORC system can realize heat recovery of waste heat resources at 70~450°C. when the heat source temperature is 450°C, the thermal efficiency can reach 27.9% [8]. when the heat source temperature is 70°C, but the thermal efficiency is only about 8% [9], the effect is not satisfactory, the cost of investment and maintenance is relatively high in the current technical conditions.

The Kalina cycle is a power cycle with ammonia water mixture as the working medium, it has higher requirements for working medium and exists pollution to the environment [10]. In order to achieve the purpose of low temperature solar energy utilization, a thermally driven electrochemical power generation device (TDEG) is applied in this paper combining a reverse electrodialysis device and a thermal separator, using ammonium bicarbonate solution as working solution, and obtaining a concentrated solution and dilute solution for reverse electrodialysis power generation through a thermal separator solution. The heat source temperature that can be used in this method is about 60°C, and the conversion efficiency is about 31% [11]. For the utilization of low-temperature heat, there is no ideal method of utilization currently.

Reverse Electrodialysis (RED) power generation technology was originally proposed by Patttle, R. E. in "Nature" magazine in 1954 [12]. The research on RED mainly uses the chemical potential difference energy between seawater and freshwater or seawater with different salt concentrations [13]. With seawater and river water as Medium, RED theoretical membrane voltage is about 80 mV [14]. Thermal Power Generation based on Reverse Electrodialysis (TPG-RED) uses a specific electrolyte solution as a medium to convert thermal energy into electrical energy, which has different application value from traditional RED. The author invented a "TPG-RED" [15] based on the theory of RED power generation technology. This paper will study TPG-RED to explore novel methods for direct solar thermal power generation.

2 The Design of Thermal Power Generation Based on Reverse Electrodialysis (TPG-RED)

TPG-RED is an innovation based on traditional Reverse Electrodialysis (RED). The basic principle of the traditional RED device is shown in the figure. The device is mainly composed of alternating and parallel installation of anion exchange membrane (AEM), membrane spacers, cation exchange membrane (CEM), cathode and positive plate, as well as pumps, pipelines and various material and liquid storage tanks and other supporting equipment. Seawater and river water are alternately passed between two adjacent membranes to form concentrated saltwater chamber and fresh water chamber arranged in turn. In the influence of concentration difference, The anion and cation in seawater are transmitted through the adjacent anion-cation exchange membrane to the river side to produce electric potential difference. The power generation system is shown in the Fig. 1.

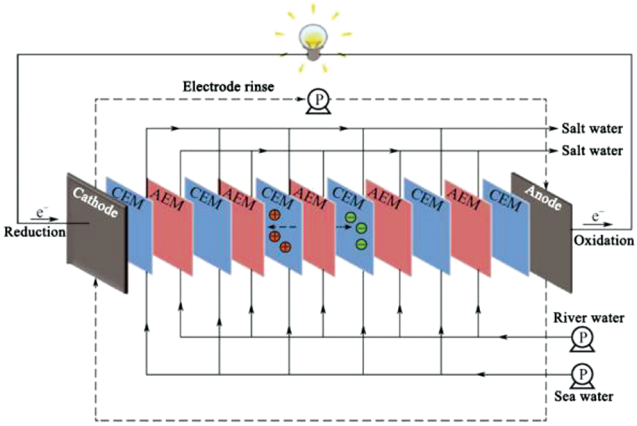

Figure 1: Schematic diagram of traditional RED power generation system

TPG-RED replaces the traditional multi-group membrane stack with a single-layer ion selective membrane between each pair of electrodes. Specific working electrolyte solution is used according to the demands of characteristics of the working electrolyte solution. In the selected working electrolyte concentrated solution, the discharge sequence of anions in water are after OH^- or the same as OH^-, such as SO_4^{2-}, F^-, NO_3^-, OH^- and so on, and the discharge sequence of cations are after H^+ or the same as H^+, such as Li^+, Na^+, K^+, H^+ and so on. The same inert electrode is used for the cathode and anode [16].

3 Experimental Device and Process of Thermal Power Generation Based on Reverse Electrodialysis (TPG-RED)

3.1 Experimental Device

Based on design ideas of Thermal Power Generation based on Reverse Electrodialysis (TPG-RED), TPG-RED experimental device is developed [17]. The experimental device is shown in Fig. 2.

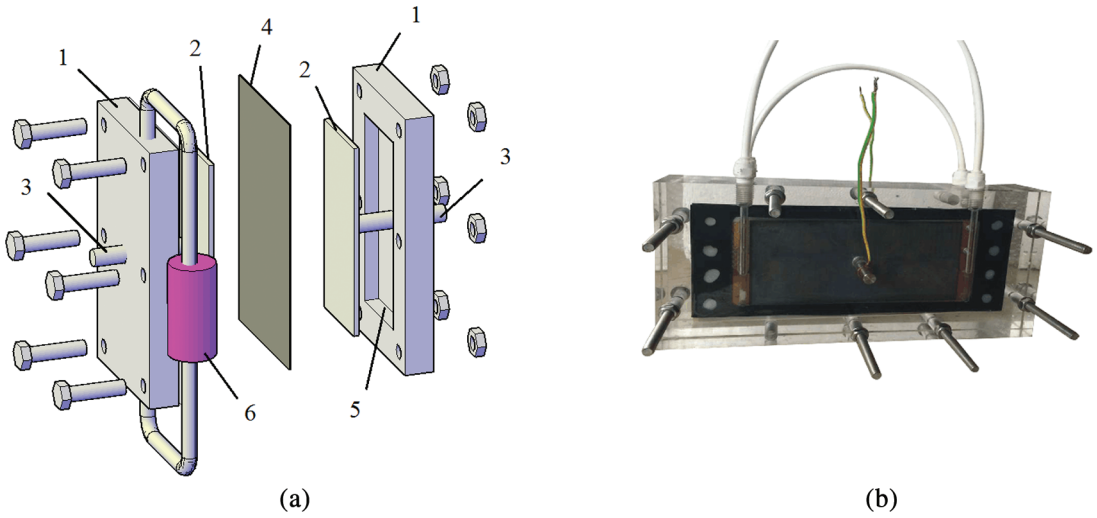

Figure 2: Experimental device. (a) Schematic diagram of the experimental device: 1—clamping device, 2—Inert electrode, 3—electrode extraction, 4—ion exchange membrane, 5—electrode chamber, 6—heat exchanger. (b) Real products picture of experimental device

The clamping device of CT-100 electrodialysis equipment is adopted in the experimental device, Both the anode and cathode electrodes are adopted with ruthenium coated titanium insoluble electrode. Only one ion exchange membrane is installed between the two electrodes, the ion exchange membrane adopts Hangzhou green environmental protection HoCEMGrion 0011 proton exchange membrane.

3.2 Experimental Process

TPG-RED can be divided into four types depending on the type of electrolyte solution: cationic acid solution, cationic salt solution, anionic alkali solution, anionic salt solution [15]. Among them, in the type of cationic acid solution, different concentrations of acid solution is adopted in the working electrolyte solution, the ion permselective membranes is cation exchange membrane. In the type of cationic salt solution, different concentrations of salt solution is adopted in the working electrolyte solution, the ion permselective membranes is cation exchange membrane. In the type of anionic alkali solution, different concentrations of alkali solution is adopted in the working electrolyte solution, the ion permselective membranes is anion exchange membrane. In the type of anionic salt solution, different concentrations of salt solution is adopted in the working electrolyte solution, the ion permselective membranes is anion

exchange membrane. Experiment of the type of cationic acid solution and the type of cationic salt solution are studied in this paper.

TPG-RED experiment: "Concentrated solution—dilute solution" using "1 mol/L H_2SO_4 solution—0.0001 mol/L H_2SO_4 solution" and "1 mol/L Na_2SO_4 solution—0.0001 mol/L Na_2SO_4 solution" respectively, making two open circuit electrode in the 30°C heat source temperature, the system converts its own thermal energy into potential energy. After 400 min, a 100 Ω load is connected between the two electrodes, and the the electric power output process is conducted.

"Effect of heat source temperature on output current" experiment: "0.5 mol/L H_2SO_4 solution—0.0001 mol/L H_2SO_4 solution" and "0.5 mol/L Na_2SO_4 solution—0.0001 mol/L Na_2SO_4 solution" are adopted, a 100 Ω load is connected between the two electrodes. After the current has stabilized, place the device in an electronic incubator to simulate the heat solar source, and different solar radiation temperatures are simulated by setting the thermostat temperature.

"Effect of concentration difference on output current" experiment: 0.0001 mol/L H_2SO_4 solution is adopted for dilute solution, 0.5, 1, 1.5, 2, and 2.5 mol/L H_2SO_4 solution are adopted for concentrated solution, change the concentration difference through the concentration variation of the H_2SO_4 solution, a 100 Ω load is connected between the poles at 30°C, the current is basically stable after 120 min, record the current after stabilization and the concentration of the corresponding H_2SO_4 solution.

3.3 Principle of Power Generation

The TPG-RED power generation principle of cationic sulfuric acid solution type is as shown in Fig. 3a, electrolyzer is divided into compartments by cation exchange membrane (dotted line), high concentration sulfuric acid solution and low concentration sulfuric acid solution are injected separately, both compartments are inserted into the same inert electrode. H^+ diffuses from the high concentration solution into the low concentration solution through the cation membrane, to make negative electricity in high concentration side, positive electrification in low concentration side, and potential difference is produced on both sides of the membrane. After the two electrodes are connected, the water molecules in the high concentration solution lose electronics ($2H_2O - 4e^- = O_2\uparrow + 4H^+$), H^+ in low concentration solution gets electronics ($2H^+ + 2e^- = H_2\uparrow$) [17]. The H^+ generated in the high concentration side diffuses again into the low concentration side to discharge. Circulated like this, the concentration difference on both sides of the membrane can be automatically maintained. When the water consumes a certain amount, the supplemental water can run continuously. Due to the diffusion of H^+, an electric field E is formed on both sides of the exchange membranes which is opposite to the diffusion direction. H^+ is affected by the electric field force opposite to the direction of diffusion, resulting the H^+ average translational kinetic energy is reduced and the system temperature is lowered, so the system converts thermal energy into electrical energy. Other types of power generation principles are shown in Figs. 3b–3d [15].

4 Results and Analysis

4.1 Thermal Power Generation Based on Reverse Electrodialysis (TPG-RED) Experiment

The open circuit voltage of TPG-RED experiment changes with time is as shown in Fig. 4a. After 400 min, the open circuit voltage of "1 mol/L H_2SO_4 solution—0.0001 mol/L H_2SO_4 solution" and "1 mol/L Na_2SO_4 solution—0.0001 mol/L Na_2SO_4 solution" was gradually increased from 0 to 28.4 mV and 0 to 31.0 mV, as shown in Tab. 1a. The theoretical value of the electric potential difference in TPG-RED can be calculated by the Nernst equation [18]:

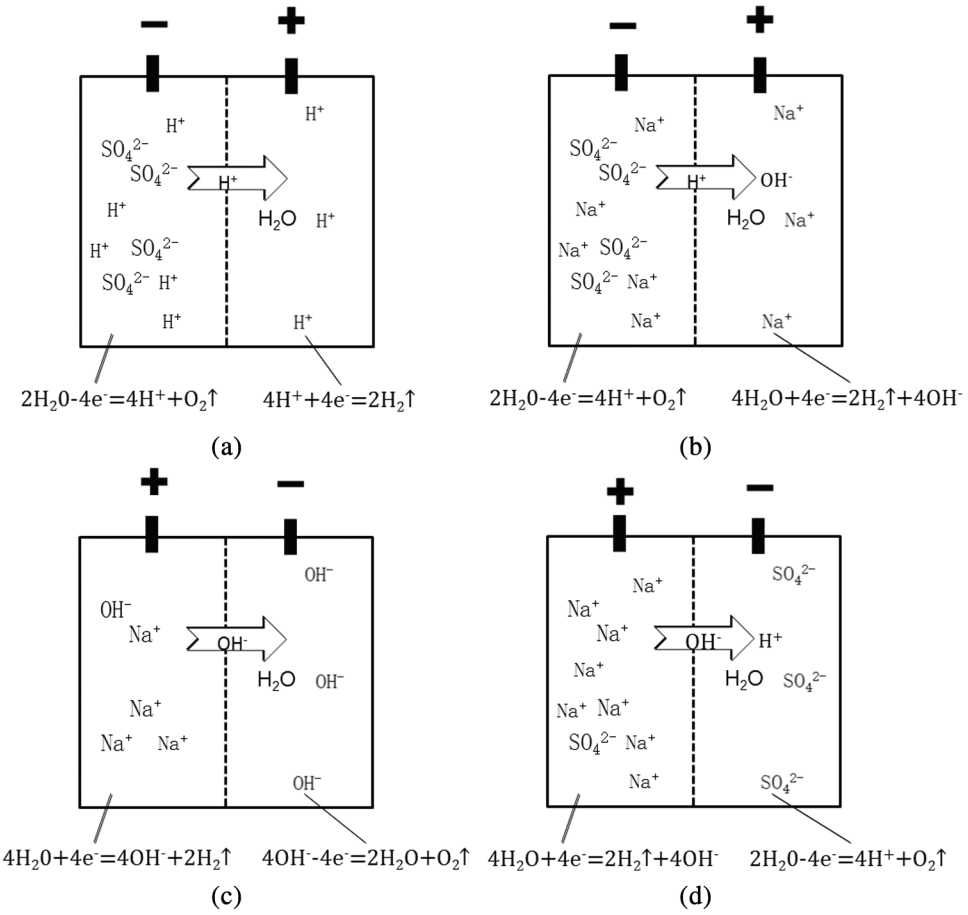

Figure 3: Schematic diagram of TPG-RED. (a) Schematic diagram of cationic acid solution type. (b) Schematic diagram of cationic salt solution type. (c) Schematic diagram of anion alkali solution type. (d) Schematic diagram of anion salt solution type

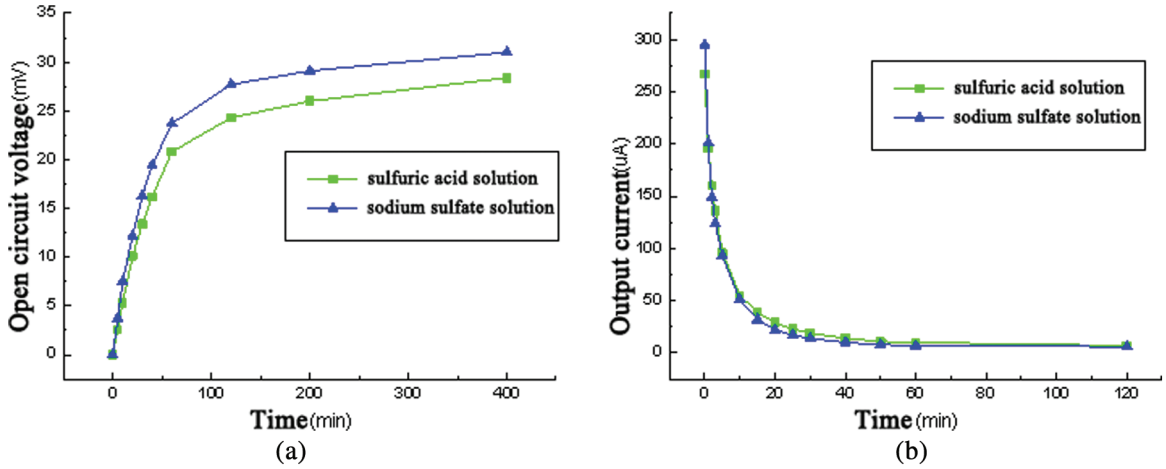

Figure 4: Curve of TPG-RED generating (a) Curve of open circuit voltage *vs*. time. (b) Curve of output current *vs*. time

Table 1: Table of TPG-RED generating

(a) Table of open circuit voltage over time

Solution Time (min)	0	10	20	30	40	50	60	100	200	400
Open circuit voltage (mv) (sulfuric acid solution)	0	2.5	5	10	13	16	20	24	25	28.4
Open circuit voltage (mv) (sodium sulfate solution)	0	3	7.5	12	16	19	23	27.5	29	31

(b) Table of output current *vs*. time

Solution Time (min)	0	2	4	6	8	10	15	20	25	30	40	50	60	120
Output current (μA) (sulfuric acid solution)	267	195	158	134	92	53	30	27	25	23	17	15	13	7
Output current (μA) (sodium sulfate solution)	295	200	150	125	90	52	27	25	24	20	15	13	11	5

$$E = \alpha \frac{RT}{zF} \ln\left(\frac{\gamma_s C_s}{\gamma_d C_d}\right) \tag{1}$$

where E is the transmembrane voltage, V; R—the gas constant, the value is 8.314 J mol^{-1} K^{-1}, T—the Kelvin temperature, α—the selective permeability of ion-exchange membranes, Subscripts *s, d* represent concentrated solution and dilute solution respectively, γ is the activity coefficient of the solution and is expressed by the following formula [19]:

$$\log \gamma = \frac{-Az^2\sqrt{\mu}}{1 + \left(a\sqrt{\mu}/B\right)} \tag{2}$$

where α is the effective radius of the ion, pm; μ—the ionic strength of the solution, mol/L; A, B are temperature-related dimensionless coefficient, the value in 25°C are 0.509 and 328 respectively. The open circuit voltage gradually increases with time and does not rise directly to the theoretical calculation value, because the open circuit voltage is proportional to the amount of ions diffused from the concentrated solution into the dilute solution, and the amount of diffused ions gradually increases with time; meanwhile, the increase of the open circuit voltage indicates that potential energy is generated during the diffusion process of ions.

The output current of TPG-RED experiment changes with time as shown in Fig. 4b. The initial output currents of "1 mol/L H_2SO_4 solution—0.0001 mol/L H_2SO_4 solution" and "1 mol/L Na_2SO_4 solution—0.0001 mol/L Na_2SO_4 solution" are 267 and 295 μA respectively. After 120 min of discharge, the output current is basically stable, 7 and 5 μA respectively, as shown in Tab. 1b. The current in the first 10 min is large and the rate of decrease is faster. Because the ion diffusion stores more net charge in the two compartments, these net charges move rapidly in the electric field generated by itself, and converting the potential energy into electrical energy. At this time, the diffusion motion in irons remain to store the net charge, but the net charge stored in diffusion per unit time is less than the net charge consumed by the power release, Therefore, the amount of net charge decreases gradually, resulting in a decrease in voltage and output current. Finally, the net charge stored when diffused per unit time is equal to the net charge consumed by power generation, the output current tends to be stable.

4.2 Experiment of the Effect of Heat Source Temperature on Output Current

This experiment explores the effect of heat source temperature on the stable output current. The experimental result is shown in Tab. 2. As shown in Fig. 5, the output current increases with the temperature of the heat source rises, because the rising temperature causes the diffusion rate to increase, resulting in an increase in the output current. At the same time, the power generation system can generate electricity from 20°C to 55°C, so the operating temperature is lower than the general thermal power generation system. The result shows a better low-temperature heat source adaptability in this power generation system.

Table 2: Table of output current *vs*. temperature

Solution Temperature (°C)	20	25	30	35	40	45	50	55
Output current (μA) (sulfuric acid solution)	2.5	3.3	4	4.5	4.9	5.4	6.2	7.4
Output current (μA) (sodium sulfate solution)	2	3.2	3.6	3.9	4.8	5.3	6	6.9

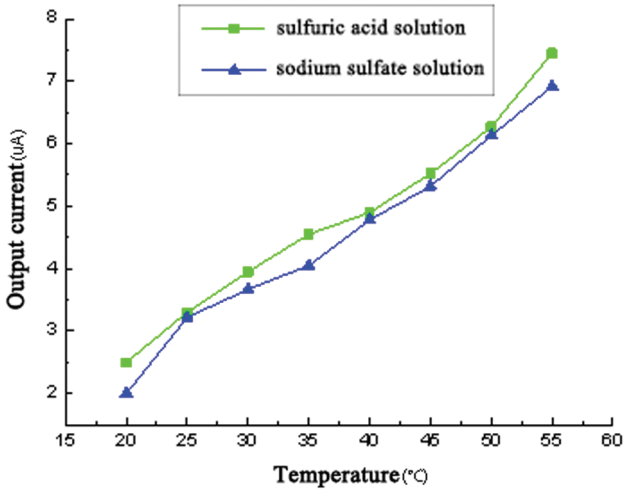

Figure 5: Curve of output current *vs*. temperature

4.3 Experiment of Effect of Concentration Difference on Output Current

The purpose of this experiment is to explore the effect of concentration difference on the stable output current. The experimental result is shown in Tab. 3, and the curve is drawn in Fig. 6. When the concentration difference (sulfuric acid concentration) is less than 1.5 mol/L, the output current increases as the concentration difference increases. When the concentration difference is more than 1.5 mol/L, the output current decreases. Theoretically, the greater the concentration difference, the faster the ion diffusion rate, and the larger the output current. However, excessive solution concentration causes damage to the ion exchange membrane, but instead reduces the output current. Therefore, the property of the power generation system can be improved by increasing the concentration difference, But there is a certain limit, the limit mainly depends on the performance of the ion exchange membrane resistance to solution concentration.

Table 3: Table of output current *vs*. concentration

Concentration difference	0.5	1.0	1.5	2.0	2.5
Output current	3.2	7	9.1	8.8	7.7

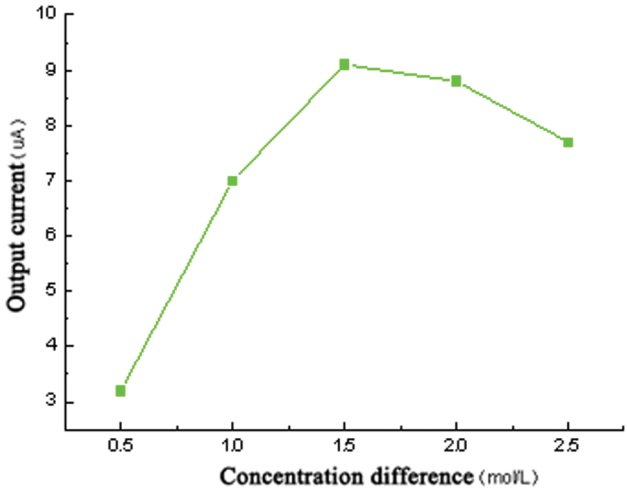

Figure 6: Curve of output current *vs*. concentration

5 Application and Discussion

Thermal Power Generation based on Reverse Electrodialysis (TPG-RED) realizes thermal power generation, especially in the case of heat sources at normal temperature to 55°C. Explored a new idea of low-temperature thermal energy generation such as low-grade industrial waste heat, geothermal energy, solar heat, and environmental heat. The further development of this technology is expected to solve the technical problem that it is difficult for traditional thermal power generation systems such as solar energy to effectively utilize low-temperature heat sources to generate electricity. The working fluid of this method can be recycled, and only to be heated to increase the internal energy of the working fluid, then the power generation system can directly convert the internal energy of the solution into electrical energy. The system possesses the characteristics of simple structure, low investment and maintenance cost, high safety and reliability, and no pollutants in the working process.

As mentioned above, the output current of TPG-RED increases as the temperature and concentration difference increase; Other studies have shown that the output power and power density of the system depend on the performance of the ion exchange membrane to a great extent [20]. The latest research shows that a nano-porous semipermeable membrane with a thickness of only 0.65 nm is used for reverse electrodialysis power generation and its power density can reach to 1 MW/m^2, which is 2000 times the power density of solar power generation, 106 times that of most ion exchange membranes on the market currently [21]. Therefore, if this semi-permeable membrane can be promoted, it will make great engineering practical potential to the TPG-RED system.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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