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Photosynthesis algal microbial fuel cell system

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Abstract

Microbial fuel cell converts chemical energy into electric energy based on the metabolism of microbe or the catalysis of biomolecules. It represents a new energy technology with many advantages, such as green and clean, renewable, low-cost and mild operating-conditions. Microalgae grow photoautotrophically by using solar energy and mainly carbon dioxide as carbon source, which are able to convert solar energy and carbon dioxide to energy storage compounds such as starch and lipids to produce food and biofuels. These features make microalgae as one cheap and reliable renewable energy resource that offering great scientific potentials.

Here, we present a photosynthetic algal microbial fuel cell (PAMFC) as a novel electricity-generation technology that utilizes microalgae as energy resource. The microalgae were in-situ grown and supplied as liquid fuel for PAMFCs. In this PAMFC configuration, novel air cathode and biological anode were developed and the performance of the PAMFC was measured. Co-C-N electrocatalyst was loaded on carbon paper, which used as biocathode. A simple process was adopted to prepare the bioanode. A theoretical short-circuit current of the PAMFC was calculated to be 0.79 mA, a short-circuit current density was estimated to be 526.67 mA/m^2, an open circuit voltage was around 0.23V, a maximum output power was 2.57×10^{-2} mW and a maximum power density is 18.31mW/m^2. The open-circuit voltage was 0.20V, which is consistent with the theoretical values.

Specifically, a recycling system was fabricated to supply microalgae solution through anode cell, therefore offering a possible practical technology for harvesting energy from biomass of microalgae.

Key words: Microalgae photosynthetic microbial fuel cell, Air cathode, Oxygen Reduction, Bioanode, Sustainable electricity generation system.

1. Introduction

Energy dilemma, water resource depletion and ecological environment deterioration have become three major factors in slowing down the development of human society. As a result, the development of sustainable energy has drawn great international attentions and concerns. Such situation makes energy science and technology a popular field in the world.

With the development of both biofuel technology and microalgal energy utilization, a novel electricity-generation technology that utilizes microalgae as energy resource called PAMFC (Photosynthetic algal microbial fuel cell) has been put forward. Basically, this system uses microalgae to storage solar energy. By absorbing solar energy, PAMFC can not only generate electricity, but also recycle energy and consume heavy metal ion within the sewage so as to control pollution. Thus, there is no doubt that this technology is one cheap and reliable renewable energy resource that offering great scientific potentials.

2. Experimental

2.1. Design &Construction on PAMFC reactors

2.1.1. Analysis on working principal and technical difficulties

The mechanism of how algal anode produce electricity is complicated. According to an existing research by Xiawu Wu[4], one possible explanation is that through photosynthesis, the algae use sunlight to convert carbon dioxide into organics. The light that algae absorb in the photoreaction stage first come to the react center of light system II, then the energy of light can release electrons, split water and turn water molecules into protons and oxygen. After that, the electron transfer on transfer chain in the membrane of thylakoid in a certain order[14]. By some conductive substances inside the solution or some attached algae, electrons can transfer onto the surface of the electrode. Bacteria or other organics mixed in the solution also contribute to produce electricity. Nowadays, there is still not enough solid evidence to prove this mechanism.

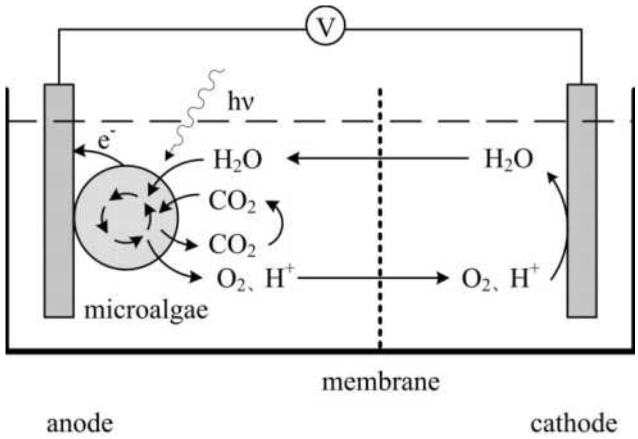

Fig 1. The structure and working principle diagram of photosynthesis algal microbial fuel cell

Base on consult a great deal of literature and datum, we started to do some experiment and basic research in the laboratory in hope of finding the truth. Here, we put forward one possible mechanism.

Inside the reactor, a diaphragm was used to separate cathode chamber and anode chamber. Seawater and algal microbial solution were pumped into cathode chamber and anode chamber respectively. Some suspending algae may adsorb on the electrode while those inert algae precipitate at the bottom. Algae gain energy through photosynthesis. Though its metabolism, the algae may generate some electronegative substance on its surface and release electrons simultaneously. Algae attached on the anode can conduct the electrons which then transfer to cathode through external circuit and drive the load. The proton transfer through the diaphragm and arrive at cathode. After that, the dissolve oxygen react with proton, generating water molecule.

One major difficulty of this process is that we should both make sure that there is enough algae to produce electrons which would transfer onto the surface of electrode and reduce the ORR overpotential of the cathode. So these are the two emphasis of our work.

2.1.2. Preparation of microalgae

We use Marine Chlorella as anodic algae, which can increase the concentration of ion in electrolyte and reduce internal resistance.

Sodium chloride solution with an average salinity of 35‰ and f/2 medium were used to simulate ocean environment. Natural daylight is also provided in order to culture Marine Chlorella. Conical flasks with a volume of 500ml or 1000ml were used as incubators while specific breathable sealing membrane were used to protect against bacteria. The incubators have to be shaken up regularly to prevent algae from precipitating.

All experiment instruments should be carefully sterilized and special equipment like UV super clean bench were used when shifting algae species. After three weeks, well-grown algal solution were selected and cultured at an extended scale. Marine chlorella adapted to the laboratory incubation condition after about one hundred days and were able to propagate largely. High density of solution were created as shown below in picture 2. a), 2. b).

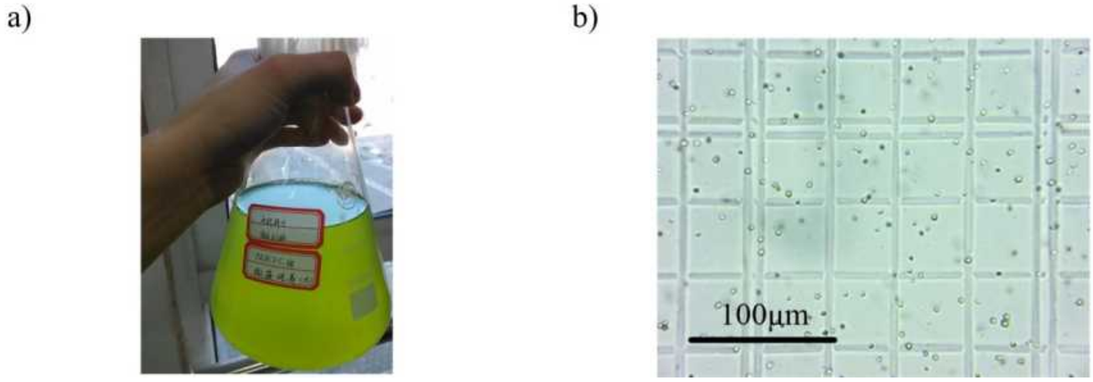

Fig 2. a) Culture of microalgae. b) Observation under microscope

2.1.3. Preparation of bio-anode

Algal microbial anode was used in this research. According to the research of Hui He, one easy way to enrich algae is to put the electrode directly in the algal solution. So we put the carbon paper into the high-density algal solution (the cultivation method has been mentioned in 2.1.1) for two days. The products were used as biological anode.

2.1.4. Preparation and characterization of air-cathode

The oxygen reduction performance of carbon paper electrode is not good enough. Both ORR potential of unmodified glassy carbon electrode and glassy carbon electrode modified by graphene are about -0.1V (vs.SCE), which suggest that these kinds of electrode are not appropriate to be used as air cathode.

According to the research of Zhiyu Yang[11], Fe-C-N catalyst has an excellent ORR catalytic activity. We also found that Co-C-N catalyst, which is always used as the material for supercapacitor, has a very good catalytic performance too.

When producing Co-C-N catalyst, we used cobalt nitrate, graphene oxide and urea as precursor to provide cobalt, carbon and nitrogen respectively. All the precursors were put in the deionized water to create solution which were stirred constantly. The product was created after dried up the solution and roasted at 900 Celsius degree, as shown in SEM below. As can be seen, cobalt particles adhere to the surface of graphene where lots of carbon nanotube grow from. We can also see that all three elements distribute uniformly in the energy spectrum, which is benefit to enlarging surface area and promoting oxygen reduction reaction.

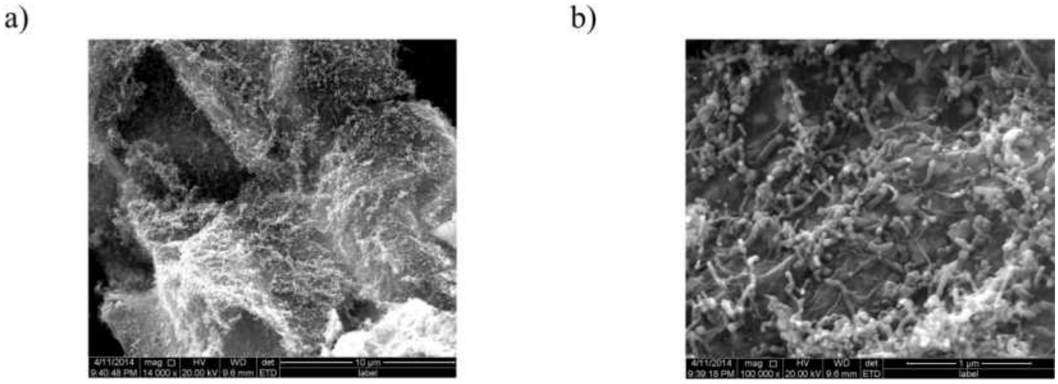

Fig 3. a) Observe Co-C-N catalyst under electron microscope with a magnification of 14000 times. b) Observe Co-C-N catalyst under electron microscope with a magnification of 100000 times

The product catalyst was dispersed in the ethyl alcohol solution which contains 15‰ naphthol. Pipette was used to coat glassy carbon electrodes with catalyst and put these modified electrode into PBS neutral buffered solution for testing performance. We can easily draw a conclusion that the ORR performance of modified electrode is much better than the original one since the ORR potential of modified electrode increased from -0.1V (vs.SCE) to 0.15V (vs.SCE), making it possible to be used as air-cathode.

Cyclic voltammetry has been tested with carbon paper electrode with a 1cm×1cm area modified with Co-C-N catalyst as shown in fig.6. Because of the increased superficial area and porosity, the current rises greatly while a slight decrease occurs in ORR potential. However, comparing to biomass cyclic voltammetry, as shown in fig.4, it’s still feasible to construct an air-cathode.

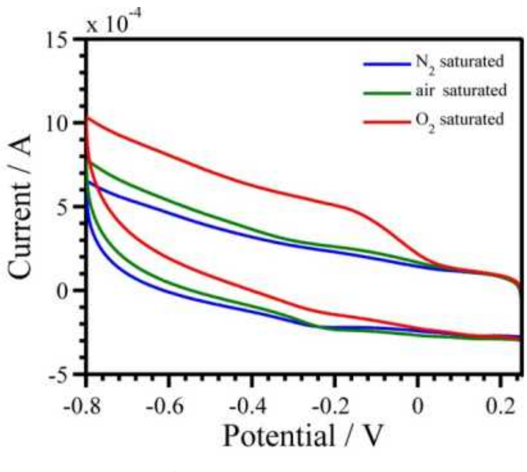

Fig. 4 CV curve of carbon paper loaded with Co-C-N catalyst

2.1.5. Construction and characterization of standard reactor

A size of 3cm×3cm Carbon papers with a sheet thickness of 0.3mm was bought from Shanghai Hesen electric appliance co. LTD. We use silver paste conductive adhesive to glue the silver wire with the carbon paper and use glue gun to fix them.

Then, the prepared carbon papers were used to construct bio-anode and air-cathode according to 2.1.2, 2.1.3. Corresponding data like polarization curves were obtained through slow cyclic voltammetry. By analyzing the curves, we predicted that expected potential should be around 0.22V.

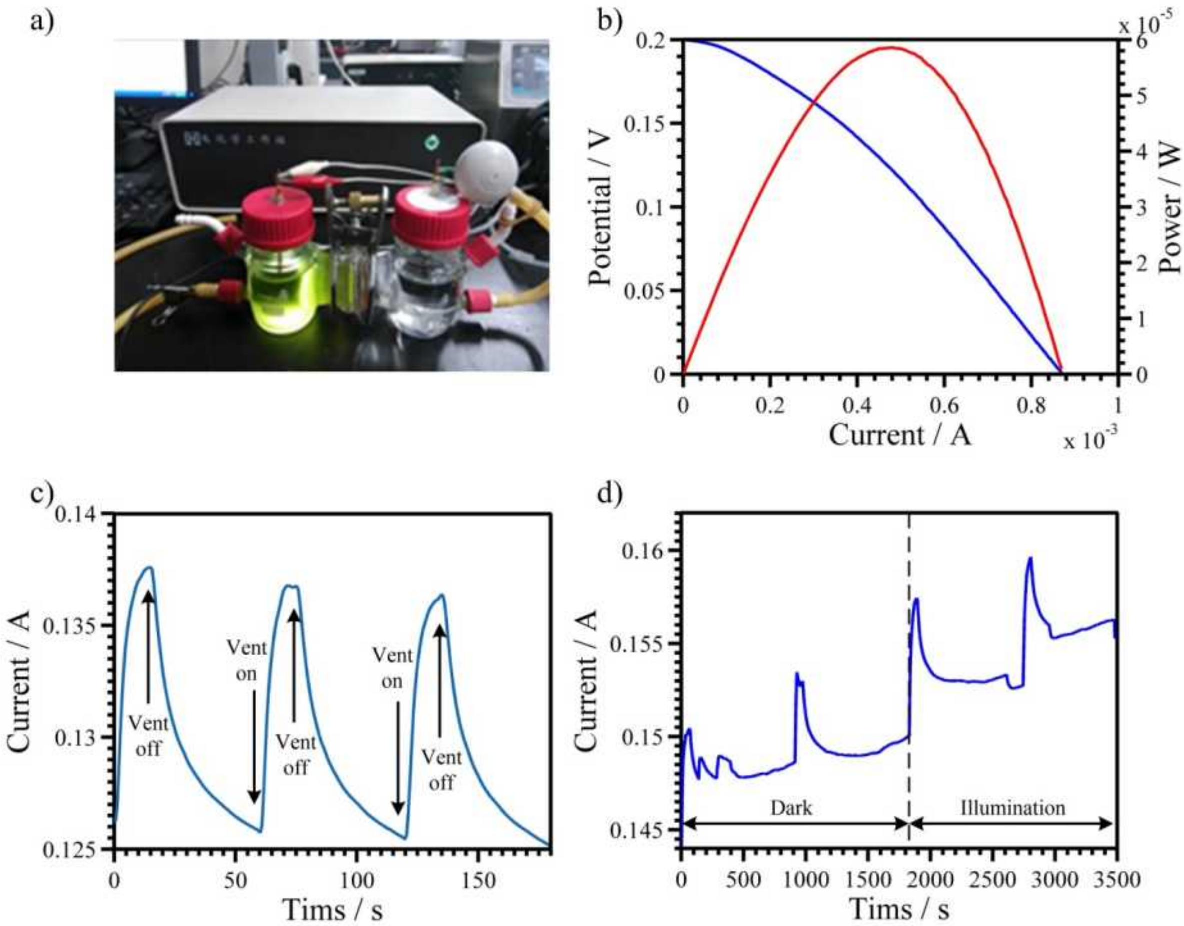

Fig 5. a) Output performance test of standard reactor. b) Actual output characteristic curves of standard reactor. c) Current responses of air-cathode when vent is on/off. d) Output response under light irradiation duration

Two flange bottles with a volume of 100ml were used as standard microbial fuel cell reactor. A specific venting device was designed and installed in the cathode part to disperse air effectively as shown in fig 5.a. Related tests were done by CHI. Open circuit potential is 0.2V, short circuit current is 9×10^{-4}mA and the max power output is 5.7×10^{-5}mW as shown in fig.10. The result is in accord with our deduction from polarization curve.

As can be seen from fig 5.d, the open potential of this battery goes up a lot when the air-cathode is pumped with air. Illumination is another factor that effect the performance of the battery. So we can draw a conclusion that the bio-anode works well and its performance has some relationship with photosynthesis. Even without light, the algae can also metabolize by consuming its own organics. This feature can stands the PAMFC out since new batteries like silicon photo cell and dye-sensitized solar cell are unable to produce any electricity in dark.

2.1.6. Optimization design & performance test of reactor

The test results prove that it’s feasible to construct fuel cell by using algal microbial.

Inherent defects of the standard microbial fuel cell reactor like high resistance, far distance between electrodes and big size contribute to a low efficiency and make it impossible to industrialize the PAMFC. Considering these shortcomings, a new microbial fuel cell reactor is designed by ourselves. This new-designed reactor that has two chambers inside is a rectangle with a size of 5.5cm, 6cm, 9cm on length, width, height respectively. Anode chamber accounts for 85% of the whole size. We also make a system to let the anode chamber to fill up or empty itself automatically so the algae can react on the anode efficiently. Gas diffusion electrode was used as cathode. Laser cutting technology are used to produce reactors. This method can both reduce the cost and ensure the machining accuracy. The product is about 100RMB each, comparing to 500RMB of the common-used standard reactor. Fig 6. a) and Fig 6. b) are the pictures of real product and the blueprint.

By testing its constant-current discharge, we know that this reactor can works at a current of 10μA, which is almost 20 times than the first generation microbial reactor. Thus, we can draw a conclusion that our design has greatly improve the efficiency.

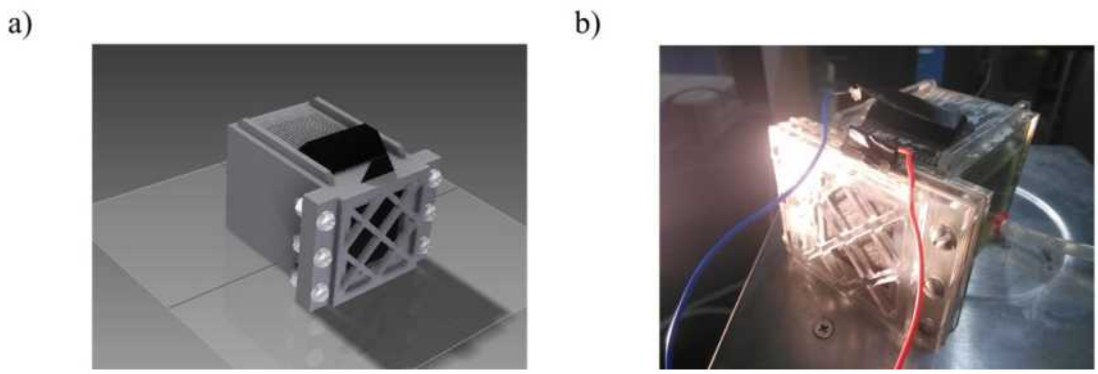

Fig 6. a) Blueprint of PAMFC reactor. b) Real product picture

2.2. PAMFC Electricity production system

2.2.1. Design of sustainable electricity production system

The open potential keeps rising slightly as the algae attach continuously to the electrode. However, the battery’s performance deteriorates when dissolved oxygen is exhausted or algae in the anode chamber degenerate. In order to avoid such situation happening, pumping fresh air to the air-cathode continuously and keeping refreshing algal solution is necessary.

Figure 6 shows our new-designed reaction system which is made up of algae solution tank, photosynthesis algal microbial reactor, photosynthesis algal microbial fuel cell reactor, ventilation device, pipelines, electrodes and external load.

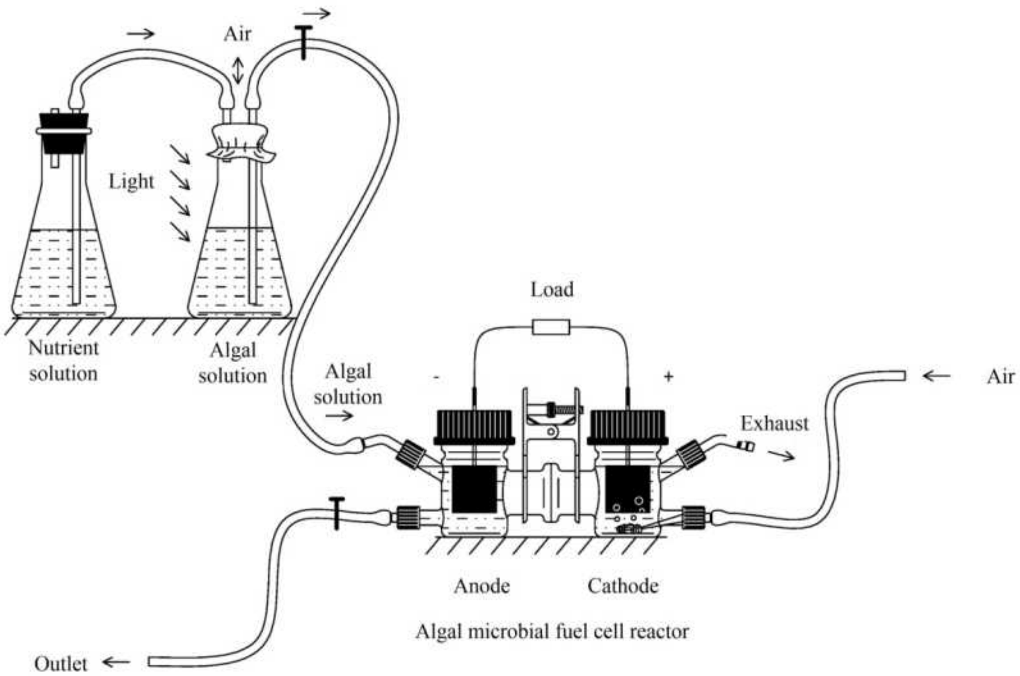

Fig 7. Blueprint of sustainable photosynthesis microalgae fuel cell system

2.2.2. Proposal of electricity harvesting

One main factor that hinder PAMFC's further development is its low output voltage. Based on that, we use a specifically designed energy harvesting nano-power management device called bq25504 to efficiently acquire and manage the microwatts (μW) to miliwatts (mW) of power generated from PAMFC. Apart from the traditional boost chip, the bq25504 starts with a DC-DC boost converter/charger that requires only microwatts of power to begin operating. The boost converter can be started with V_{IN} as low as 330 mV, and once started, can continue to harvest energy down to VIN = 80 mV. The system can output a voltage of 3V or 5V after storing energy. The bq25504 also implements a programmable maximum power point tracking sampling network to optimize the transfer of power into the device. Sampling the VIN_DC open-circuit voltage is programmed using external resistors, and held with an external capacitor (CREF). On top of that, the storage element ensures that constant power is available when needed for the systems.

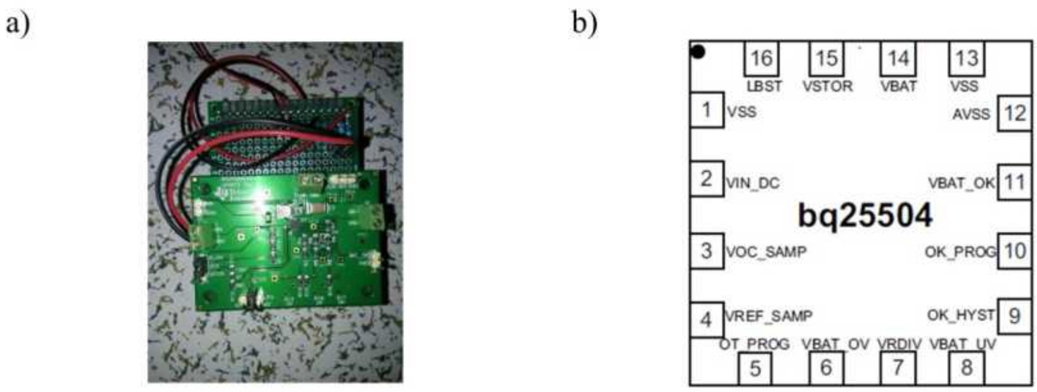

Fig 8. a) Texas Instrument BQ25504EVM. b) Texas Instrument BQ25504 chip pin figure

Our single battery is unable to drive the circuit so we connect several reactors in parallel. Once the circuit is working, an output voltage of around 2V can be obtained stably, which is enough to drive most common electronic devices. We parallel the reactor with a supercapacitor. Thus once the supercapacitor is charged with over 80mV, it can charge another supercapacitor or drive loads directly.

2.2.3. Design of PAMFC electricity production system

The PAMFC demonstration system is based on “2.2.1 sustainable electricity producing” and be adjusted and improved accordingly to fit our self-designed reactor. Energy harvesting system, algal solution cycling wireless control system and output monitoring system are added as shown in fig 9.

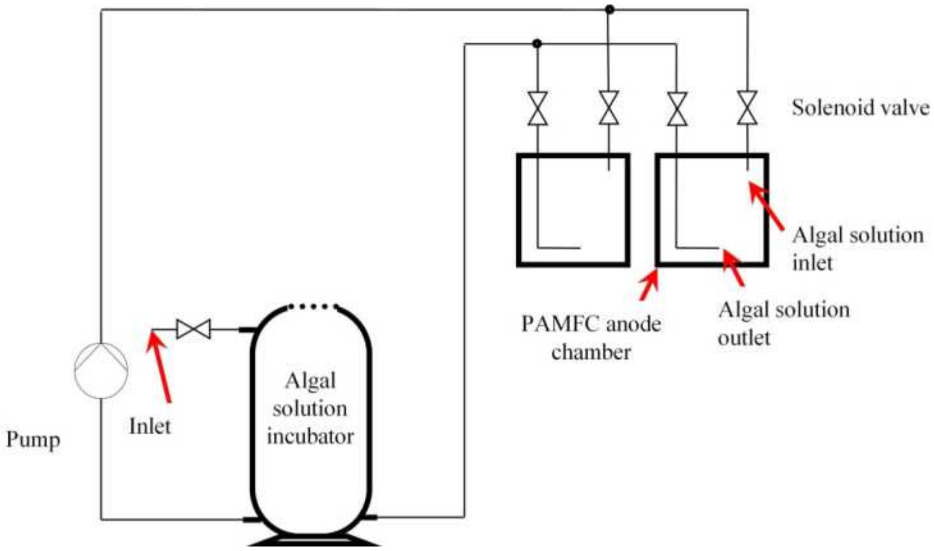

Fig 9. Design of small-scale microalgal solution cycling system.

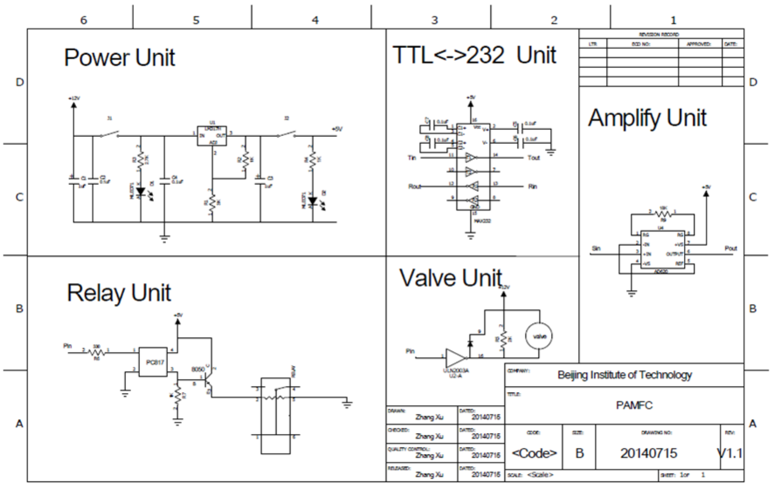

Fig 10. Design of circuit in electricity production

Firstly, we use diaphragm pump to transfer the algal solution which has already been cultivated in the container into the reactor. The activity of the algae decreases as the reactor works so solenoid valve has to start regularly to keep updating the solution. The used algal solution is then pumped back to the container and grow under lighting radiation.

Research shows that organic waste inside industrial effluents, ammonia-nitrogen waste water and other waste can be treated as nutrition sources. So by utilizing the nutrition in that waste water, our PAMFC system can both recycle energy from sewage and achieve energy & greenhouse reduction.

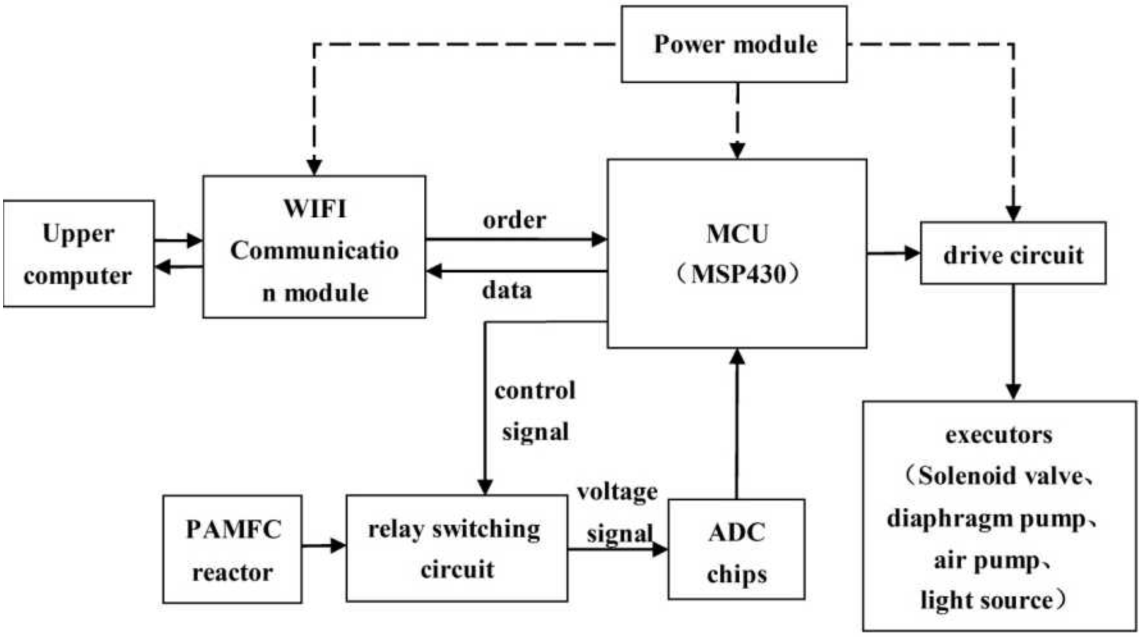

Fig 11. Control system in PAMFC demonstration system

To keep the whole system working, we designed and created an automatic remote control system. Personal computer are used as remote monitor and upper controller while a wireless network module is equipped to transmit and receive signals. Fig 10 is the design drawing of our circuit and fig 11 shows our system overall layout. Fig 12. a) and Fig 12. b) show designed picture and real product respectively.

a) b)

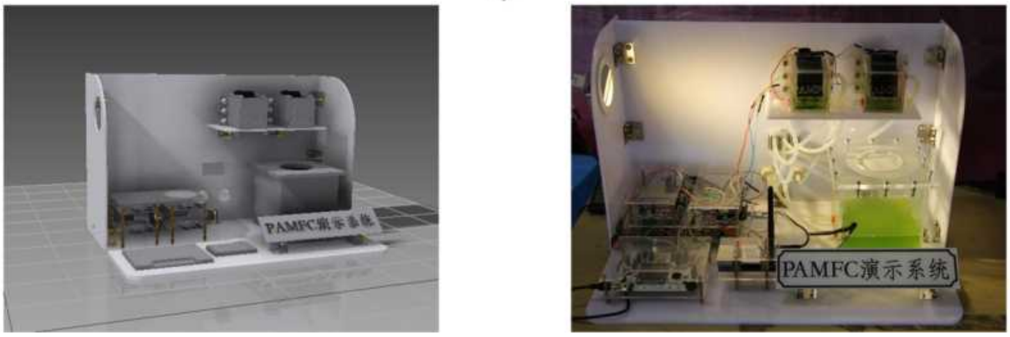

Fig 12. a) Blueprint of PAMFC demonstration system. b) Picture of PAMFC real product.

3. Conclusion

Based on the intrinsic characteristics of PAMFC system, we put forward its utilizable prospects.

Large-scale algal electricity producing base can be established in remote sea area and island. Since our reactor can generate 1mW electric energy in a reaction volume of 1 cubic decimeter, 1W electric energy is predicted to be generate in a reaction volume of 1 cubic meter. Thus, a large-scale reactor is suggested to be built up in some remote area to produce electricity.

Since the reactors might have different size, it can output various amount of electricity to support environmental monitoring system, beacon, etc. Furthermore, we build up an automatic control system and wireless communication module in consideration of remote area as it may be. We hope operators can control the whole system at anywhere through our user interface with internet in the future. The PAMFC is not only reliable and simple, but also free from combustion, explosive, irradiation and other dangerous situation that traditional method have. The only consumption in the system is algal solution. However, the algae can keep reproducing to supply the need. Generally, our system is easy to operate and fix.

The innovation point of our research is building up an algal microbial fuel cell, optimizing the whole system and designing a sustainable electricity-producing system. We put forward a new idea using remote wireless control on sea algal power production.

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