INDIAN INSTITUTE OF TECHNOLOGY, GANDHINAGAR

ES-415: Project Report

Bioinspired Catalysts for renewable energy/Energy harvesting

Under the guidance of
Prof. Raghavan Ranganathan

Submitted by
Umang Agarwal
Patel Vashisth

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Acknowledgement

We would like to express our special thanks to Prof. Raghavan Ranganathan, who gave me the golden opportunity to do this project on the topic “Bioinspired Catalysts for renewable energy/Energy harvesting”. It helped us in doing a lot of research, and we came to know about so many new things.

1. Introduction

With increasing global energy demands and the harmful effects of traditional fuels, the world is transferring to renewable energy sources and energy harvesting technologies. Energy generation from sunlight, wind, water, etc., is among the most popular renewable energy sources. As the technologies are transiting to renewable energy systems, many challenges are associated with energy generation, storage and efficiency of processes.

Here we will discuss a new approach to solving modern-day problems associated with renewable energy: to take inspiration from nature. The field of nature-inspired materials is growing with time. The most important advantage of nature-inspired material designing is that nature has already been exposed to many challenges of renewable energy generation. The whole life cycle on Earth runs through renewable energy sources, i.e. the sun.

The article focuses on bioinspired catalysts for renewable energy and energy harvesting. Bioinspired catalysts are synthetic catalysts designed based on natural catalysts found in biological systems such as enzymes. These catalysts are designed to mimic the structure and function of the natural catalysts found in biological systems. Catalysts are essential and responsible for increasing the rate of reactions (here, reactions related to renewable energy production). There are many ways of using bioinspired catalysts for renewable energy harvesting, which are discussed in the following article.

2. Types of Bioinspired Catalysts

2.1 Enzymatic Biofuel Cells

Enzymatic biofuel cells are special devices which have several uses in the field of biomedicine and environmental applications. They have sustainable production of energy from biofuels even at mild operating conditions which makes it a great application.

In an EBFC, glucose and oxygen act as the fuel and oxidant for the reaction. Here, glucose oxidase oxidizes at the anode by glucose oxidizing enzyme, leading to the production of hydrogen ions (H+), gluconolactone, and electrons (e-). The reaction is as follows:

$$\text{Glucose} + H2O + O2 \rightarrow \text{Gluconolactone} + 2\ H+ + 2\ e-$$

The electrons go from anode to cathode through the circuit leading to the reduction of oxygen to water by the help of the enzyme laccase. The reaction is as follows:

$$O2 + 4\ H+ + 4\ e- \rightarrow 2\ H2O$$

The overall result is the conversion of glucose and oxygen into gluconolactone, water, and electrical energy, which can be utilized in various applications.

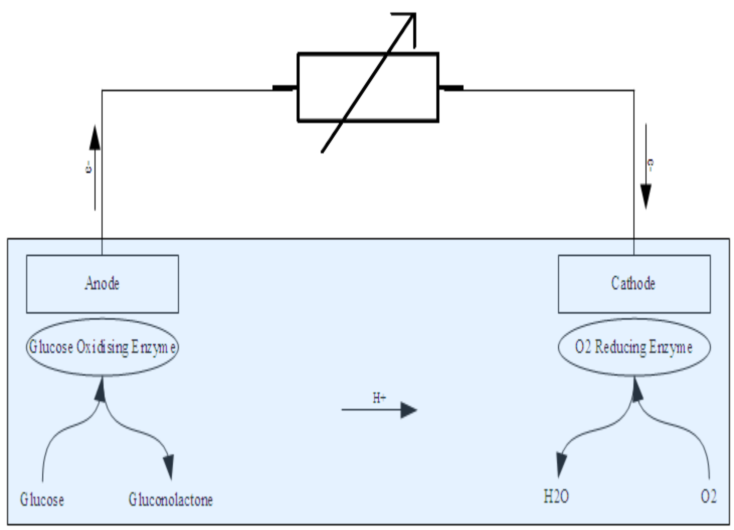

Fig.1 Schematic diagram of enzymatic biofuel cell.[1]

Enzymatic biofuel cells have been designed to emulate the intricate mechanisms by which living organisms derive energy from biochemical reactions. In line with the cells of living beings, enzymatic biofuel cells harness the potency of enzymes as catalysts to transmute chemical energy into electrical energy. Additionally, the selection of enzymes utilized in enzymatic biofuel cells is frequently influenced by natural systems. For example, glucose oxidase and laccase are enzymes that occur naturally in fungi and bacteria, where they partake in organic compound metabolism. By exploiting these enzymes in biofuel cells, researchers can exploit their natural proficiencies to effectively transmute organic compounds into electricity.

In the field of biomedical applications, enzymatic biofuel cells are found to be of great use in implantable medical devices such as pacemakers, and biosensors. Employing biocompatible and renewable fuels, like glucose or other naturally-occurring sugars, presents a promising avenue for attaining a stable and enduring source of energy for these instruments. The mild operating conditions of EBFCs also make them more compatible with biological systems than traditional batteries or other power sources, which can be corrosive or toxic. Additionally, the selectivity of enzymes used in EBFCs can provide specificity for the target fuel, potentially reducing the risk of side effects or interactions with other biological molecules.

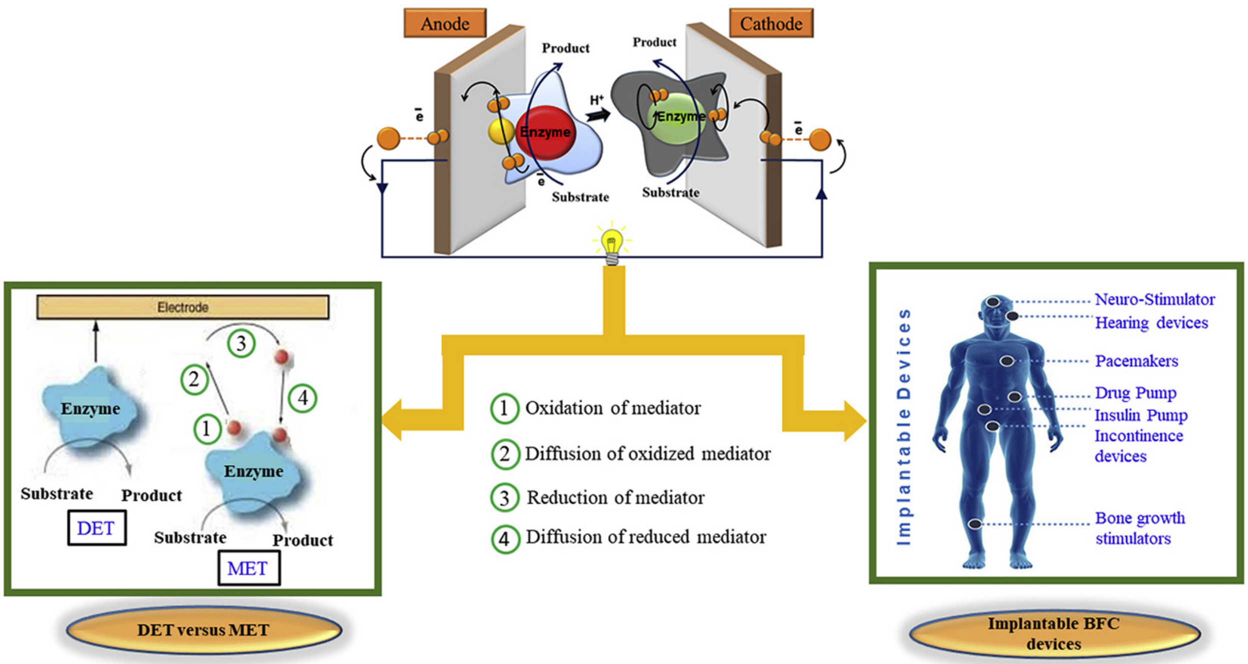

Fig.2 Functioning and Biomedical use of EBFCs[2]

In the environmental field, EBFCs have been investigated for use in wastewater treatment, where they can help to remove organic contaminants and generate electricity at the same time. Enzymatic biofuel cells can also be used in remote or off-grid areas where traditional power sources are not available or practical. This can include environmental monitoring devices or remote sensors. Enzymatic biofuel cells are also scalable and cost-effective, making them a good option for many environmental applications.

2.2 Photosynthetic Biohybrid Systems

Photosynthetic biohybrid systems are an innovative and promising renewable energy technology that seeks to mimic the natural process of photosynthesis. By harnessing the power of photosystems, which are networks of proteins and pigments that capture light energy and convert it into an electron flow, these systems can generate electrical energy from living photosynthetic organisms or their components.

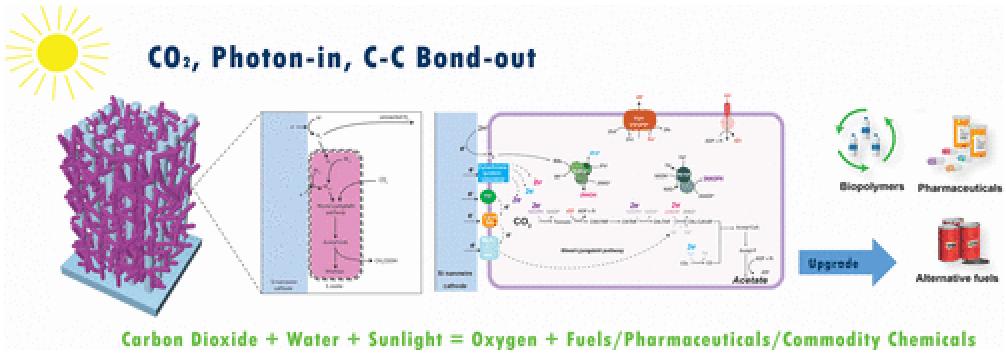

Fig.3 production of liquid sunlight through a "photon-in, chemical bond-out" mechanism[3]

Photosynthetic biohybrids use a complex interface between materials and biology to convert photons into chemical bonds, creating a liquid sunlight known as 'photo-in, chemical bond-out mechanism'. This process can be studied through various methods, such as spatiotemporal imaging, spectroscopy, transcriptional, and proteomic analyses. The interface between the materials and biology spans multiple orders of magnitude in length and time scale, making it a challenging subject to probe.

This Photosynthetic Biohybrid System is mainly inspired by the Photosystem II which is the most crucial unit of photosynthesis. Photosynthesis in plants basically consists of two photosystems found in the thylakoid membranes of chloroplasts in plant cells which are photosystem I (PSI) and photosystem II (PSII). PSII is the first to act, despite being named second, and both photosystems consist of an antenna complex and a reaction center. Photosystem II captures light energy and uses it to oxidize water, generating oxygen, protons, and electrons. The antenna complex comprises pigment molecules that capture photons and transfer the energy to the reaction center, where chlorophyll molecules initiate electron transfer via an electron transport chain. This process produces ATP and NADPH, which drive carbohydrate synthesis.

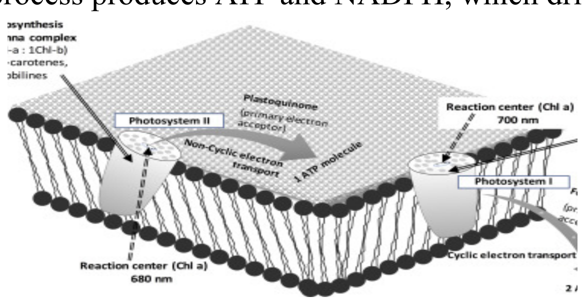

Fig.4 PS-I and II in the thylakoid membrane[4]

A photosynthetic biohybrid system usually has two parts: a light-collecting section and a reaction section. The light-collecting section typically uses man-made materials such as nanomaterials, polymers, or dye molecules to gather and transfer light energy to the reaction section. The section where reactions occur consists of biological components that have the ability to utilize the captured light energy to trigger targeted chemical reactions, such as reducing carbon dioxide, splitting water, or synthesizing organic compounds.

They have the potential to revolutionize renewable energy and energy storage applications, potentially disrupting the conventional solar power systems. They are in high demand and light due to their captivating properties because they can directly produce chemical energy from solar energy which can be stored for later use. Apart from that, it is cost-effective along with its potential scalability and eco-friendly friendly nature which makes it an ideal source for energy generation in the coming future.

2.3 Biomimetic membranes

One of the unique ways of energy generation is to generate electricity from the salinity gradient between the river and the sea. At the places where the river meets the sea, the ionic concentrations in the seawater are far higher than that in the river water. Due to this, ionic movements occur. This movement of ions can be used to produce electricity.

There are two approaches for energy generation from the ionic gradients present, 1) Pressure-related osmosis and 2) Reversed Electrodialysis(RES). In pressure related osmosis technique, the membrane is put between the high and low salt regions, which can permeate water but not ions. This leads to mechanical energy generation because it can be captured by changing pressures with time. In the RES process, the ions are selectively permeated through the membrane to achieve the movement of ions, which changes potentials on both sides of the membrane. The potential change is used as a medium of electron transfer in the outer circuit, which has two ends connected to the media on both sides. The RES process largely depends on the selectivity and permeability of the membranes. The selectivity here refers to the tendency of the membrane to let only specific types of ions pass through it, and the permeability refers to the number of charges passing through the membranes.

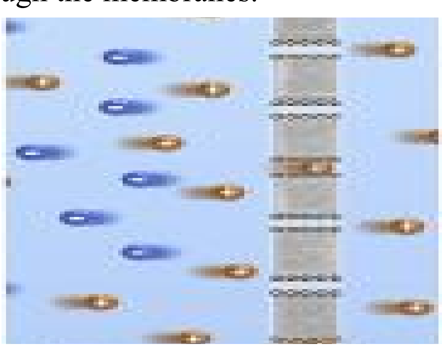

Fig 5 Design of traditional symmetrical membrane.[5]

The traditional membranes are made with surface charges to increase both the selectivity and permeability of ions through membranes. For example, if we want to pass positive ions through the membranes, then the membrane surfaces are negatively charged, increasing the concentration of positive ions on the membrane. The increased concentration leads to a greater flow of positive ions through the pores. However, there are certain challenges associated with the traditional technique. One problem is that the selectivity and permeability are inversely related. To increase the selectivity of ion permeation, the pore sizes are decreased, which reduces permeability and vice-versa. Another challenge associated with traditional membranes is that both the surfaces of the membranes are made of the same material, which essentially leads to the same charged surfaces. The presence of the same charge on both sides leads to the accumulation of the permeated charges on the other side of the membrane; this is called the counterion effect. This hinders the permeation.

Recent progress in RED-based energy harvesters suggests using heterogeneous membranes for electricity generation. The structure of these membranes is inspired by ion exchange in the Eel cells. Eel produces electricity in its body to hunt prey and to avoid hunters. The cells responsible for electricity generation in Eels are called electrocyte cells. These cells have different K+ and Na+ ions concentrations on either side of the cell membrane. Whenever there are external stimuli, the membrane selectively permeates these ions to generate a potential difference, generating electricity.

The structure of these ion channels is shown below,

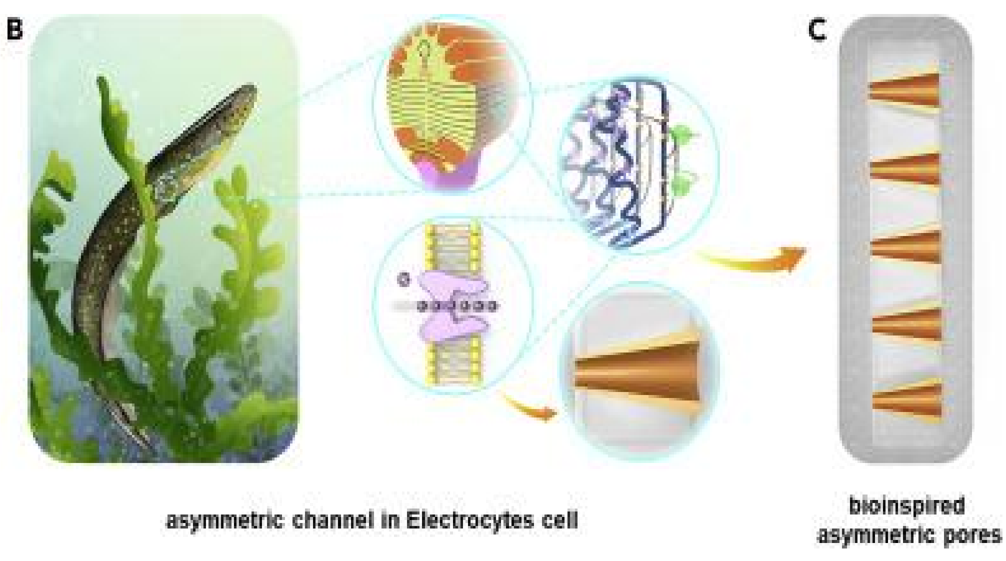

Fig 6 Structural feature of cell membranes in Eel and an example of the bioinspired membrane.[5]

As we can see from the image, the K+ ions and other ions are abundant inside the cytoplasm of the Electrocyte cells. The pore size gradually increases from inside to outside to selectively permeate the ions outside when the ion channels are opened. This helps in the increase of selectivity as well as permeability. The other property of the membranes is that the membranes have different types of charges on either side. This leads to the efficient transfer of ions without generating counterion effects. The biomimetic heterogeneous membranes(Fig 6) are then formed, having two membrane surfaces joined together. The one with smaller pores was joined to the high salt concentration, and the other was on the river water side. The surface charges on these membranes were also altered to make the permeation of charges through the membrane more efficient.

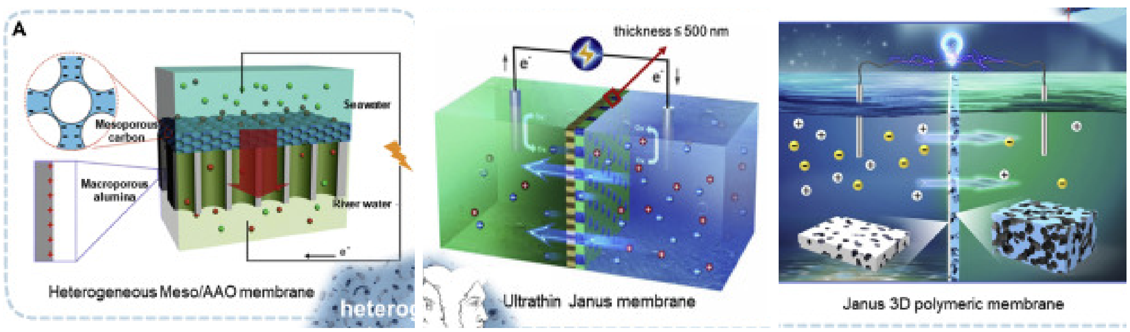

Fig 7 Nature-inspired heterogeneous membranes.[5]

The power density reached in the case of the leftmost membrane case is 3.46 W/m2. The power generation needed for the sustainable application of the technology is 5.0 W/m2. In the second case, the film thickness decreased to 500 nm, contributing to relatively higher permeability and power generation. The power generated was 2.04 W/m2. Furthermore, in the last case, when the asymmetrical distribution of the ions was done on the membrane film, the power generation was increased to 2.66 W/m2.

From the observations, we can see that the bio-inspired structure had a very high power generation capacity, and the one with the Eel type structure in the leftmost figure with changing pore sizes and charges on either side of the membranes was the one with the highest power generation. These membranes' power generation is higher than the traditional symmetrical membranes. This is an example of the potential of biomimetic membrane structures. However, long-term stability, scalability, cost-effectiveness and many other parameters must be considered for practical application.

2.4 Bioinspired Electrocatalysts

Electrocatalysts are the materials which facilitate reactions happening in fuel cells. They influence the rate of the reaction and make the process faster. One of the most important reduction reactions related to the fuel cell is Oxygen Reduction Reaction(ORR). The most commonly used catalysts for the ORR are noble metals, especially platinum. As noble metals are costly and rare in nature, the overall functioning of fuel cells becomes costlier. Another problem with the oxygen reduction reaction is the kinetics associated with the reaction. ORR reactions have slower kinetics, because of which the platinum loading at the cathode is generally higher. So it becomes highly important to find a cheaper replacement.

Oxygen reduction reactions are abundant in nature. Many bacterias, plants, and algae have oxygen-reduction reactions for energy production. Different enzymes catalyze the ORR in these organisms; one of the most prominent enzymes is Laccase. The Laccase is made of two copper ions surrounded by complex polymer chains. Figure a in the below figure shows the structure of the Laccase.

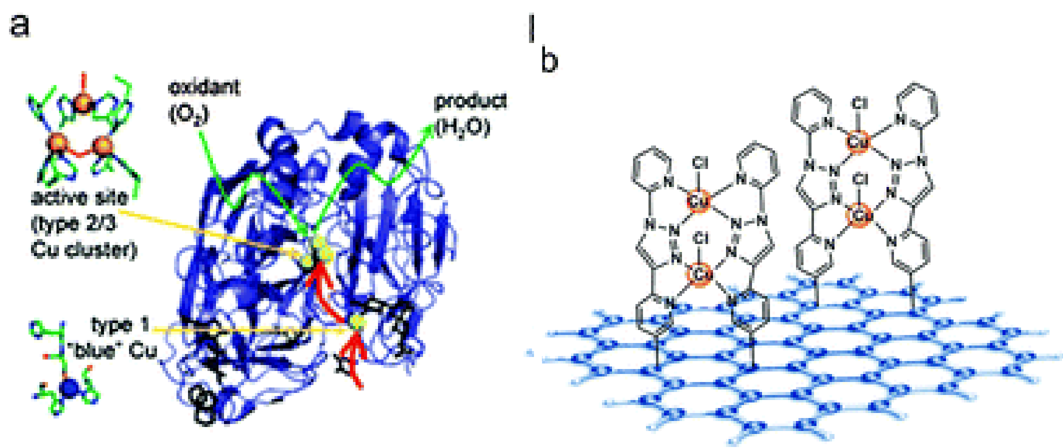

Fig 8 a) Structure of Laccase and b) Laccase-inspired enzyme.[6]

The b figure in the above figure is a biomimetic structure inspired by Laccase. The material has to be used as a cathode on the electrochemical cells. The reduced graphene oxide sheet is covered by motifs having a similar structure to that of Laccase to make a cathode for the reaction. The motifs are copper complexes with ligand triazole-dipyridine(TADPy) joined to a graphene oxide sheet with covalent bonding. If the motif is replaced with one copper ion or more than two copper ions, the reduction efficiency decreases drastically and if the number of copper ions is two, then the cathode functions with the optimum efficiency. The material shows a good oxygen reduction ability.

Following are some of the reasons we draw for the success of the material for the oxygen reduction reaction:

- The reduction reaction happening on the cathode is,

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$$

The two oxygens are first separated and then are reduced to form water. The presence of two copper ions required can be because of the presence of the need to require two oxygens at the same time. The overall reaction may not be possible on one copper ion, so two copper ions in one complex structure are required.

- The oxygen reduction ability of other metals, such as iron, is greater than copper. However, iron and other metals tend to form a bond with oxygen which is relatively lower in the case of copper. Copper can transfer electrons to oxygen without reacting with it.
- The presence of large legends is also important, as, without the presence of legends, the copper can come in direct contact with oxygen, leading to copper oxide formation. The presence of legends does not let oxygen come in contact with the copper directly so that only electron transfer happens and the structural integrity is maintained.

These are some of the reasons for the structural features of the rGO-TADPuCu cathode, which we think are associated with oxygen reduction ability. Again, the structural stability, scalability and control of ORR are challenges associated with the electrode structures. However, the structure shows a high potential for research and should be researched further.

3. Summary

The bioinspired catalysts have shown very promising properties comparable to the current materials. Using these structures in energy applications, especially renewable energy, has a high potential for real-world applications. The enzymatic biofuel cells have a huge potential for biomedical applications. They can be used as autonomous powering sources for biomedical devices, which can use bodily chemicals to function. Photosynthetic biohybrid systems can also potentially produce energy from water or CO_2. The potential for a photosynthetic system is huge, as sunlight is one of the most abundant energy resources. In the case of biomimetic membranes, we have discussed that their unique application in generating energy at sea and river interfaces is quite fascinating. The potential use in the future can also be ineffective water purification and filtration usage in medical applications. Bioinspired catalysts can replace platinum electrodes used in the ORR. They can even be used for controlling the reaction, which is very difficult for ORR.

Although there are diverse applications of bioinspired catalysts and the future scope is also broader, the current state of research in many cases is at the primary stage. Extensive research is needed to achieve all the potential applications. The long-term stability of catalysts, the production of practically hierarchical structures, and the large-scale production of elements are some of the many challenges biomimetic catalysts face. Incorporating existing technologies to improve the newly developing bio-inspired technology is also challenging.

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