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Thermal Influence on the Semiconductor behaviour of Organic Materials

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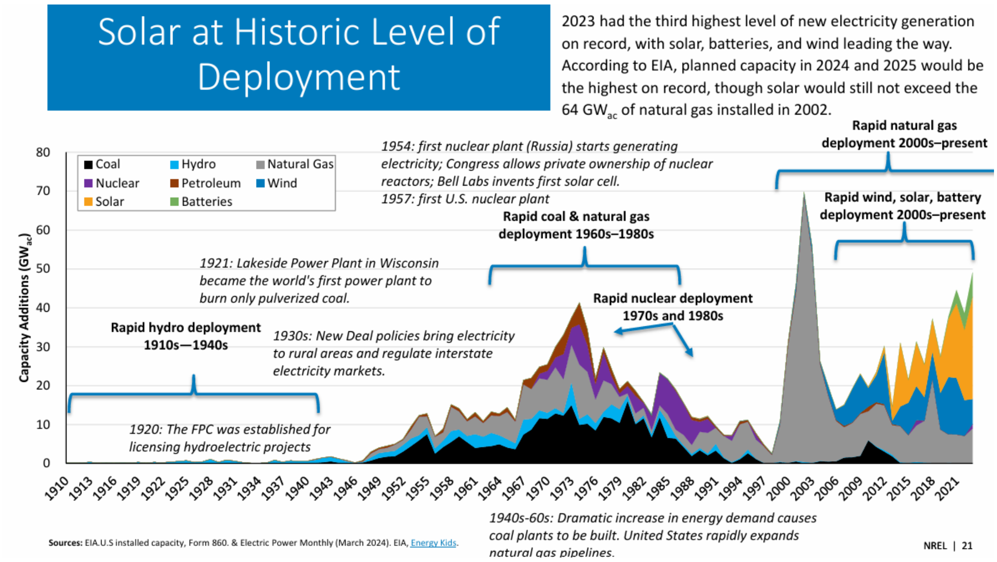
ABSTRACT

Organic solar cells (OSCs) are the most promising alternative sources of energy as they can play an important role in generating clean and cheap energy [1]. The design for organic Solar cell is single organic material or composite of organic materials are placed between two electrodes. One electrode with lower work function worked as Cathode and other one as Anode. To generate exciton in organic layer light should be reached up to organic semiconducting layer, keeping this point in mine one electrode must be transparent in nature.

Keywords: *Thermal Influence, Organic Materials, OSCs, Electrodes, Semiconducting Layer.*

Introduction

After long time research now, we are in a phase where organic semiconducting material or dyes are used as active layer. Organic solar cells (OSCs) are continuing the solar cell design trend of creating devices through inexpensive processing/printing techniques that make tuning and optimization more feasible [2]. Tang in 1986 prepared a solar cell in bi-layer cell design which exhibited 1% efficiency, which revolutionized the technology [3]. in 1991 Gratzel and O'Regan research work was based on Dye Sensitized Solar Cell (DSSC) , which was very attention seeking topic in solar cell research field. Initially in 1991, DSSC achieved efficiency of 7.1-7.9 %, and more recently in 2005 efficiencies reached to 11% [4, 5].



Solar at Historic Level of Deployment

2023 had the third highest level of new electricity generation on record, with solar, batteries, and wind leading the way. According to EIA, planned capacity in 2024 and 2025 would be the highest on record, though solar would still not exceed the 64 GW_{ac} of natural gas installed in 2002.

1954: first nuclear plant (Russia) starts generating electricity; Congress allows private ownership of nuclear reactors; Bell Labs invents first solar cell.
1957: first U.S. nuclear plant

1921: Lakeside Power Plant in Wisconsin became the world's first power plant to burn only pulverized coal.

1930s: New Deal policies bring electricity to rural areas and regulate interstate electricity markets.

1920: The FPC was established for licensing hydroelectric projects

1940s-60s: Dramatic increase in energy demand causes coal plants to be built. United States rapidly expands natural gas pipelines.

Sources: EIA.U.S installed capacity, Form 860. & Electric Power Monthly (March 2024). EIA, Energy Kids.

Fig. 1: Progress in Solar Cell Technologies

High surface area of active layer increases the more photon harvesting which increase exciton generation and use of suitable dye to utilise the maximum range of solar spectrum to absorb, these two factors are main key features for efficient solar cell. Excitonic Solar Cells (XSCs) is another name for Organic Solar cells. The year wise progress of solar at Historic level of deployment is shown in Fig.1. Though OSCs possess efficiency much lower than other technology, their low cost makes them strong competitor of other technologies. OSCs with their low cost can make passive recharging of consumer electronics and energy production for remote locations where their light weight is essential for ease of transportation.

Organic Semiconductors

In organic solar cell organic materials are used as active layer. The main properties of organic material which makes them suitable for organic solar cell is their conducting nature and charge carrier transport ability. In 2000 Prof. A. J. Heeger got the Nobel Prize in field of Chemistry to study conducting and semiconducting properties of organic materials with the accidentally iodine doping of poly-acetylene. This was a milestone discovery. The chemically doped polyacetylene (Fig.2.) had a conductivity of 10^5 Sm^{-1}. This accidentally discovery initiate the research in many other fields of organic electronics. Conjugated π-electrons system in different dyes, pigments and liquid crystals is a part which is responsible to transport charge carriers. The high conductivity in these materials is based on conjugated π-electrons.

Fig. 2: Chemical Structure of Polyacetylene

In chemistry the alternate single and double bond forms a conjugation in carbon compounds. If we see the basic chemical structure of Polyethene and polybutadiene we can easily understand the alternate single and double bond conjugation system. To understand it we explained it in Fig.3, in this fig. orbital overlapping diagram of ethene shows the conjugated π-electron structures. Carbon has the ability to form σ and π bond with another carbon atom. The electron associated with σ bonds are σ electron and with π bonds are π electrons. The π electrons are loosely bound with atom and they can easily move along the π bond. Opto-electronic is because of movement of π electron.

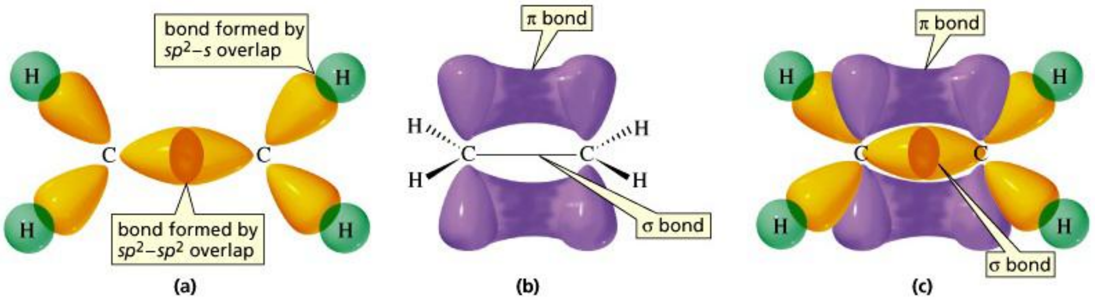


Fig.3. (a) Orbital structure of Ethene, both carbons are sp^2 hybridized, the first carbon-carbon σ bond is formed by sp^2-sp^2 overlapping carbon orbitals, while the second σ bond is formed by interacting hybridised sp^2 of carbon and unhybridized s orbitals of Hydrogen. (b) carbon-carbon π bond is formed by unhybridized p-p overlapping of orbitals, Delocalisation of π-electrons. (c) Merged orbital structure of ethene.

Semiconducting Behaviour in Organic Material

Hydrocarbons are carbon and hydrogen compounds. Carbon has a property of catenation; it can formed bond with itself and form a long chain easily. Hydrocarbons are again categorised in to two category saturated hydrocarbon and unsaturated hydrocarbon. A neutral carbon atom is tetravalent and has six electrons giving a ground state electronic configuration of $1s^2$, $2s^2$, $2p^2$. In saturated hydrocarbon compound carbon form single bond with another atom. To form four bonds, in carbon atom outer electron from $2s^2$ promoted to 2p vacant orbital. In excited electronic configuration $2s^12p_x^12p_y^12p_z^1$ all orbitals are with single electron. In saturated hydrocarbon all four orbitals will hybridised and ready to form single σ-bond with another atoms. σ-bonds are strong bonds and their electrons are not able to move freely in chain of bonds; they are localised electrons. The energy gap between LUMO and HOMO orbital are very large so they are insulator compounds.

In unsaturated hydrocarbons carbon either form three σ-bonds and one π-bond or form two σ-bonds and two π-bonds. Hydrocarbon with two σ-bonds and two π-bond are named alkyne, these compounds have linear geometry and formed π bonds are in cylindrical form so they are not able to conduction or movement of electron throughout the bond. Special class of hydrocarbon with three σ-bonds and one π-bond are named alkene, they are planner compounds with three sp^2 hybridised orbital in a carbon atom. Three hybridised sp^2 orbitals formed three σ-bonds and one unhybridized-pure *p* orbital is ready to overlap side by side to another atom with pure *p* orbital. The *p-p* orbital overlap side by side formed π bond, this is the key for conductivity in organic compounds. The π bond electrons are loosely bound electron and π bond is weak bond, so π electrons are delocalised between two atoms. As the single and double bond comes in regular alternate fashion the delocalisation of π electrons throughout the conjugation increases. The band gap between LUMO and HOMO can also be tailored and changed.

The organic semiconductors used as active layer in organic solar cells are a class of material made by carbon compounds. In this class of unsaturated hydrocarbons carbon atoms are primarily sp^2 hybridised with trigonal planner geometry. Unlike traditional inorganic solar cell active materials are inorganic semiconductors as silicon and germanium, these semiconductors have π conjugation system. The electrons in these π-bonds are more loosely held and are delocalized over the conjugated system. This delocalization of π-electrons allows them to move relatively freely along the molecular backbone, making electrical conduction possible. The mobility of these π-electrons is significantly higher than that of the localized σ-electrons, which is why the π-conjugated system is essential to the functionality of organic semiconductors.

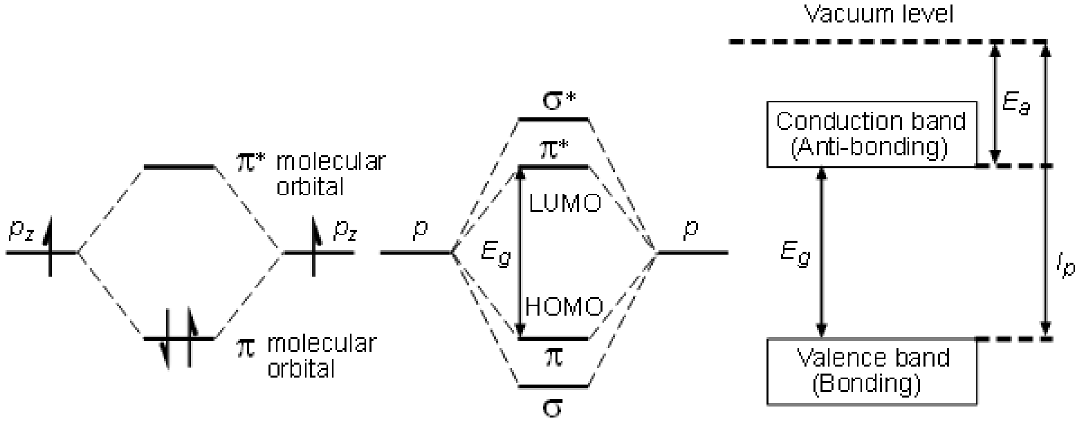


Fig.4. Schematic representation bond formation through overlap of orbitals. Unsaturated hydrocarbon compounds with Lowest Unoccupied Molecular Orbital (LUMO) Conduction and Highly Occupied Molecular Orbital (HOMO) valence band.

The ability to control electron delocalization through molecular design enables organic semiconductors to be tailored for specific electronic and optoelectronic applications, such as in OLEDs, OPVs, and OFETs.

The orbitals of atoms overlap each other to form a long chain or alternate single and double bond in organic semiconductors. These overlaps of molecular orbital form a continuous band with some energy value. The highest energy level up to which electrons are filled named as Highest Occupied Molecular Orbital (HOMO) with some finite value of energy. The vacant orbital overlapped band with lowest energy termed as Lowest Unoccupied Molecular Orbital (LUMO). These both levels have some finite energy value difference: Energy gap (E_g), Electrons are required to gain energy from outside or from another source equal to this value to excited electron jump from HOMO to LUMO. One possible way to conduction or transportation in organic compound is possible only when energy gap (E_g) value very lower, so that on room temperature electros are able to jump from HOMO to LUMO easily. Another one we dopped gust molecule which have energy level in between host materials HOMO and LUMO level. This energy level of guest can work a platform to jump electron from HOMO to this level and favour conduction in organic materials.

Orbitals in LUMO level can also responsible to accept electron and Fig.4. shows band structure of an organic molecule. Energy levels of these band also characterized as namely electron affinity (E_a) and ionization potential (I_p). Electron affinity is the energy value released by gaseous atom when electron received in LUMO level of atom or corresponds to the lowest state of the conduction band (π^* orbital). Same as Ionisation potential is the energy value released when electron removed from gaseous phase atom from outermost orbital represented by I_p , valence band (π orbital) and corresponds to the highest occupied molecular orbital (HOMO).

In Organic semiconductors the Energy band gap lies between ~ 1.0 - 4.0 eV. This range of energy band gap also suitable to absorb the spectrum in infrared to ultraviolet region. For efficient Solar cell the selection of active material depends upon that the energy gap matched with the range of spectrum to enhance absorption and conduction of charge carriers.

Temperature Dependence Semiconducting Behaviour

Organic semiconductors have poor charge carriers transport properties and large band gaps. Also, in organic semiconductors the binding energy of excitons is quite large (~ 0.5 eV) compared to that in inorganic semiconductors (~ 0.01 eV). To determine the efficiency of solar cell the efficient absorption of photon and diffusion of excitons are primarily focused aim and both are depending upon the thickness of active layer of organic layer. The exciton once formed must be diffused up to interface between donar and acceptor organic layer. With good diffusion length of exciton in organic layer promote efficient photovoltaic cell. Poor charge transport properties and large exciton binding energy results in the small diffusion lengths and short life-time of the charge carriers. Temperature plays a crucial role in the behaviour of semiconducting devices, significantly influencing their electrical characteristics and performance. In organic layer Excitation of electron from lower energy level to higher energy level ca be done with increase in temperature of device, this favour the charge conduction in organic layer. This increase enhances the conductivity of intrinsic semiconductors, but in doped semiconductors, the overall conductivity can decrease due to reduced carrier mobility. Higher temperatures cause increased lattice vibrations (phonons), which scatter charge carriers more frequently, thereby lowering their mobility. Additionally, elevated temperatures result in increased leakage currents, especially in devices like diodes and OSC's, which can lead to greater power dissipation and reduced efficiency. In OSC's, the threshold voltage typically decreases with rising temperature, potentially affecting the stability and switching behaviour of the device. Another significant concern is thermal runaway, particularly in bipolar junction transistors (BJTs), where a rise in temperature can cause increased current, generate even more heat and potentially lead to device failure. Over prolonged periods, high operating temperatures can accelerate material degradation and reduce the lifespan of semiconducting devices. Therefore, thermal management is critical in the design and application of semiconductor-based electronics.

Temperature Dependence behaviour in Organic Solar Cells

Current-Voltage characteristics in semi-log scale are shown in Fig.5. These measurements are done in dark and in illumination form, temperature varied from 299-120K. In dark when no illumination done shows that no excitons are formed current only due to injection of carriers through electrodes. The current in dark reduces with decreases in temperature, current in forward bias current reduces more compare to current in reversed bias. This indicate the charge transport property is temperature dependent in organic layer. In the reverse bias (+ve voltage to Al) the current became almost temperature independent below 250 K. Temperature independency of the current below 250 K in the reverse bias suggests that the current might be controlled be the tunnelling of the charge carriers through large injection barriers [6]. The current shows ohmic behaviour at 299 K in the reverse bias. This ohmic behaviour in the reverse bias can probably be attributed to the high charge injection barriers in the reverse bias [7].

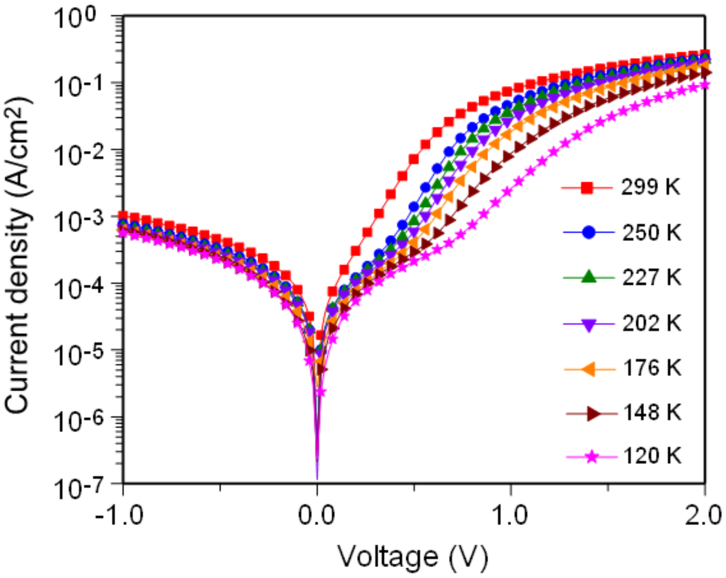


Fig. 5: Dark *J-V* Characteristics

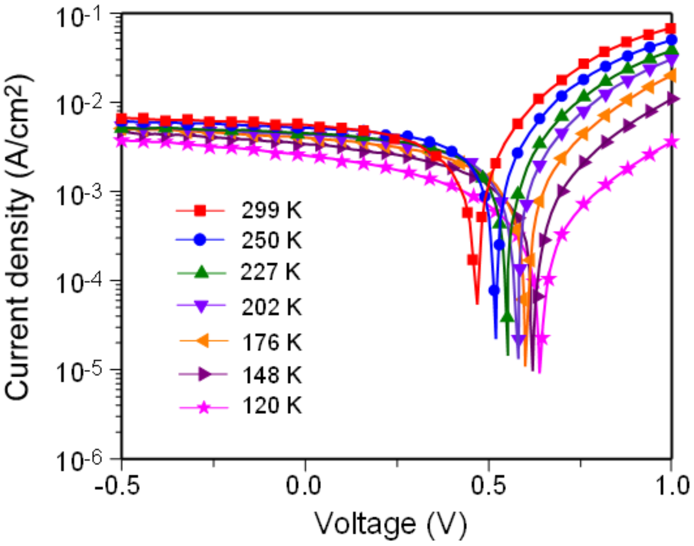


Fig. 6: Illuminated *J-V* characteristics

For excitation from lower energy level to higher energy level electrons are require energy, this energy can easily gain through elevation in temperature. With low temperature Ohmic behaviour shows that carriers which have no sufficient energy to overcome barrier can easily travelled through tunnelling. It favours that the reverse bias current in the present OPV device is following tunnelling mechanism at low temperatures. The illuminated *J-V* characteristics is shown in Fig.6. with temperatures variation on a semi-log scale. The current value of device seems to reduces in illuminated as well as dark condition. As we reduce the temperature current value reduces significantly. Fig. 5 shows the effect of temperature on J_{sc} and V_{oc}. A reverse pattern observed in J_{sc} and V_{oc}, the J_{sc} decreases while V_{oc} increases with the lowering in temperature. The graph behaviour is linear for both J_{sc} and V_{oc}. This behaviour can be explained on the basis of nature of organic semiconductors. Organic semiconductors are non-crystalline and they have lots of traps.

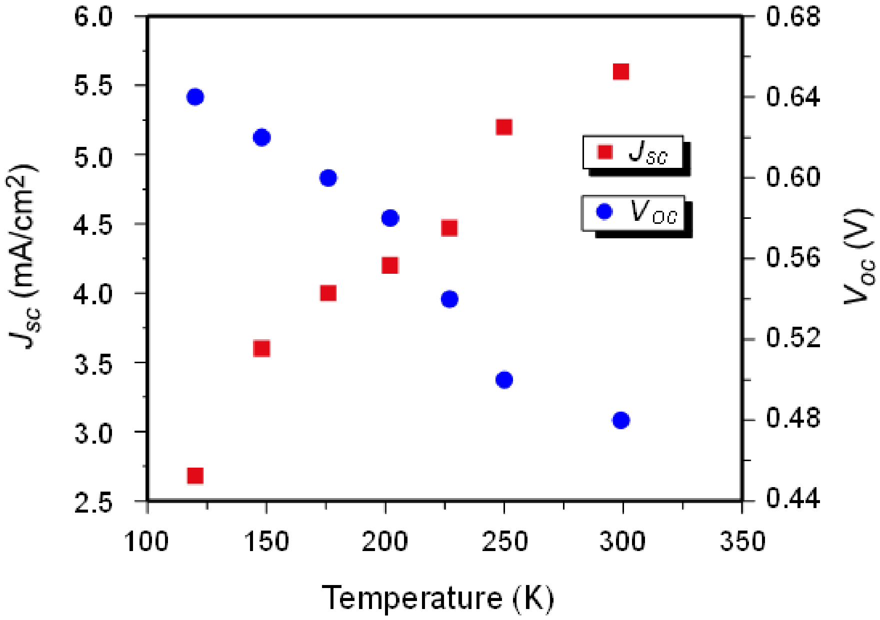


Fig. 7: Variation of V_{oc} and J_{sc} as a Function Temperature

Morphology of Organic material is amorphous. The charge carriers are captured by these traps so the mobility is lower and with reduction in temperature the current value again reduces due to electron have no sufficient energy to overcome these traps and jump from HOMO to LUMO. So, the electronic transport properties of organic semiconductors are strongly depending on temperature. Charge carrier mobility of Organic Semiconductors reduces with lower temperature. J_{sc} reduces with lower temperature the active organic materials. One would expect that the lowering of temperature will reduce the current [8]. Trapping effect and lower charge carrier mobility both favours the reduction in J_{sc} with temperature.

To explain dependency of V_{oc} on temperature, we have to understand mechanism of Organic Photo Voltaic Cell. Basic structure of OPV shows that Organic Semiconducting Material (Active layer) coated over transparent ITO (anode) and another side a metal electrode as cathode. Generally, we coated a low work function Matal layer as cathode. When these three layers comes in contact the Fermi level alignment takes place, this is the equilibrium state for energy level of all layers. This alignment of fermi level creates an electric field in device; this is known as built in electric field. This electric field drive the electros and holes towards respective electrodes. Electrode toward cathode and holes toward anode. The electrodes also have some work function value, the difference of work-functions of two electrodes is known as the built-in voltage (V_{bi}).

In equilibrium the alignment of fermi levels of active layer and work function difference of electrodes generate an electric field inside the active layer of Organic Photovoltaic cells. The charge carriers accumulate on electrode changes the built-in voltage (V_{bi}). Temperature variation affects the mobility of charge carrier and directly affects the V_{bi}. Alternatively, the temperature dependence of the V_{oc} (Shown in Fig.7.) in the present case has been attributed to the temperature dependence of built in voltage (V_{bi}). Depending upon the electrodes, V_{bi} can be as high as ~ 1.3 V [9]. The contact between organic layer and metal electrode is become Ohmic contact by apply a exciton blocking layer between organic active layer and metal electrode. For the present study these contacts are assume to Ohmic. Mihailetchi *et al.* [9] showed that in the vicinity of the Ohmic contact a significant band bending occurs due to accumulation and diffusion of charge carriers. This band bending produces a significant loss in the V_{bi}. Kemerink *et al.* [10] used a simple analytical model to study the effect of temperature on the band bending. It has been shown that the band bending at the electrodes depends upon temperature and decreases with reduction in temperature. Temperature has a direct effect on the diffusion, which decreases with reduction in temperature. The reduction in diffusion results in the reduction in the curvature of the band edge. The reduction in band bending at low temperatures results in the increment in V_{bi}. It is well known that the V_{oc} has direct dependence on V_{bi}. Therefore, the reduction of temperature results in the increment in V_{oc}.

Conclusion

In charge carrier the temperature has a significant effect and overall important parameter to device performance. In reverse bias the Dark current was less sensitive to the temperature compared to the forward bias current. The dark current under reverse bias and at low temperatures is governed by the tunnelling of the charge carriers through large injection barriers whereas under forward bias it is dominated by diffusion. J_{sc} decreases while its seems that V_{oc} increases in inversely with temperature. With temperature reduction bend bending increases and its effect on V_{oc} reflected in graph, showing reduction in V_{bi}. As temperature reduces J_{sc} also reduces this is reflected the dependency of charge carrier mobility on temperature.

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