Urea - Hydrogen Compost Soil Microbial Fuel Cell for Multifunctional Applications

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Research

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Abstract

Background: This paper provides an overview of the present advances in renewable and sustainable energy resources used for new energy demand in the world. Aiming to address, Urea, Urine resources are abundant like urea-containing wastewater, industrial urea, wastewater treatment plants, becoming an attractive option as anodic fuel for the application in urea fuel cells. And as a hydrogen-rich chemical fuel, urea can also be hydrolysis and electrolyzed to produce hydrogen for energy storage in the near future.

Results: We report a novel, urea-hydrogen based compost soil microbial fuel cell (UH-CSMFC). As compost soil is a rich source of bacteria, enzymes, and organic matter, soil provided the necessary ingredients for the operation of the device. While bacteria and enzymes that hydrolysed by urea powered by the fuel cell. The compost soil was also found to exhibit partial electrocatalytic activity itself. This novel UH-CSMFC shows power density of 18.26 mW/m^2. For continuous operation of the device, and cleaning of the excess of nitrogen compounds from urea fuel (urine, containing different wastewater energy resources).

Conclusion: The constant state is the most desirable, where the device behaviour is entirely irreversibly, which helps to feed the device. Thus, the results of electrochemical studies show that the system is suitable for cleaning, hydrogen, power generation by consuming urea as fuel. This multifunctional device is sustainable, cheap, and eco-friendly for the environment.

Background

The rapid increase in power consumption and various environmental issues have compelled the research community to identify new sources of renewable energy [1] Microbial fuel cells (MFCs) use bacteria or secreted enzymes to break down fuel for power generation. In MFCs, bacteria and enzymes act as biocatalysts for the oxidation and reduction reactions that produce electricity in the compost soil systems [1–6].

Almost all the liquid MFCs have associated safety concerns, quickly degraded very fast due to volatilization of ammonia, mainly related to toxicity, shifting, and leakage problem. Therefore, compost soil is preferred for minimizing the risks, and less fuel and get more work and more power as compared to the liquid state. Furthermore, the reliable sources are usually cheaper and pose no issues with volatilization; moreover, it is easy to maintain the pH levels in the soil as solid-state [7–11]. Among all the available resources of sustainable energy, urea is a suitable fuel for MFCs. It is an advantage that in the natural processes of nitrification and denitrification in the nitrogen cycle by compost soil microbes during their growth. We propose using stable compost soil, and urea rich waste as fuel for storing the energy. Compost soil acts as a mediator, ionic conductor, separator and a source of electro-genic bacteria, which supply additional nutrients to the microbes. It is a complex system containing water, mineral, and bacteria, which is also beneficial for the plants.

The other advantages of the stable system are the availability of reliable and leakage proof systems, which are easy to handle. The bulk size design has many advantages for power and maintenance. Easy refuelling with abundant urea waste fuel in bulk size and can prepare stacks for the power generation in series and parallel easily at a higher rate which is not possible in the coin cell reported before. Its has a novel approach for generating green energy at a large scale in coming future by using any type urea riche waste as fuel. [11–16]

The success of the hydrogen economy requires a safe, efficient, and environmentally friendly method for hydrogen production. Standard methods for hydrogen production generate substantial greenhouse gases (steam reforming) or require significant electrical energy input (water electrolysis). The electrochemical oxidation of urea to hydrogen in alkaline media has significant benefits over standard hydrogen production methods. Urea rich wastewater is widely abundant and currently purged into rivers and lakes where it undergoes a natural conversion to ammonia. Ammonia was released in the gas phase to Earth's atmosphere resulting in billions of dollars in health costs each year [17–24].

As an energy medium, a critical factor is the low thermodynamic potential of urea (0.37V) in comparison with water (1.23V) to release hydrogen for controlled delivery to presumably energy-producing device [2, 5]. In this case, hydrogen is typically released thermally or with hydrolysis. There is also a great possibility of directly retrieving energy from urea with high efficiency to complete the carbon and nitrogen recycling. Besides, another primary urea source is naturally from urea or urine rich wastewaters and other wastewater treatment plants containing the urea content, which is often leading to eutrophication [5, 6]. Those urea/urine wastewaters can be treated through an oxidation reaction to release nitrogen gas before their discharge into environments or even turned to recycle water after further treatment to reduce the health costs and cleaning and generating energy from the waste through soil processes [6, 25–30].

Therefore, urea electrolysis offers multiple benefits with the direct conversion of urea to valuable hydrogen, which has not been accomplished with any other technology up to date it's a novel concept, despite many advantages of urea treatment technology, which are either associated with the production of hydrogen electricity and recycle clean water from urea rich sources. But Still, there are many problems, in liquid-based hydrogen storage urea fuel cell and but after keeping the same liquid fuel pass through compost process with a massive amount of micronutrients present bacteria, urease enzymes present in them so that fastly work being done as the soil is a natural source of microbes to grow in the soil is their home too for easily survival soil is help fuel for maintaining the constant temperature which is helpful for the growth of microbes at room temperature. [7, 31–38].

Herein, a urea-hydrogen compost soil microbial fuel cell (UH-CSMFC) uses naturally collected urea as a fuel in the compost soil using functional graphite electrodes for hydrogen collection, power generation, and environment cleaning, as shown Fig. 1 is the MFC electrochemical testing was for different urea concentrations. Additionally, the utility of this multifunctional urea-hydrogen storage based compost soil MFC was realized to reduce the urea rich water toxicity in the soil, and try to decrease the soil pollution, water pollution these all are environmental pollution [4, 5, 39–46].

Results And Discussion

Catalyst characterization and performance

The I-V measurements were performed from (0 to 28) hours cycle to study the electrocatalytic activity of UH-CSMFC, which is shown in fig. 2. To avoid any unnecessary electrochemical reaction by the metal catalyst and to promote stability, the same material (Graphite) was used as an anode and cathode. For continuous operation of the device, and for cleaning of the excess of nitrogen compounds from wastewater, the constant state is the most desirable, where the device behaviour is entirely irreversibly, which helps to feed the device.

From fig.3 (a) and (b), it confirms the catalytic activity for both the samples as Fig. 3(a) showing the comparison between fuel 0.5g/ml in a liquid state urea hydrogen microbial fuel cell (UH-MFC)and UH-CSMFC with urea fuel 0.5g/ml for checking the performance between them. The potential redox peak for urea bipolar CV measurements was in the range of 0 to ±1, similar to the values reported in the literature. The catalytic activities were found to be at ± 0.1 to 0.6 V range for urea and ± 0.5 V for the ammonium ions [5]. Both urea and ammonium ions are related to each other as sources of nitrogen and as fuel for accelerating the process of power generation used this time [3, 4, 9-12].

As shown in fig.3 (b), the EIS difference between the two samples. EIS measurements were performed to investigate further the electrochemical behaviour of the compost soil were real, and imaginary impedance studied in the frequency range from 0 Hz to 10,000 Hz for the applied field. Shows the electrocatalytic activity study by using bipolar CV measurements with the comparison of the urea liquid state UH-MFC and the effect of UH-CSMFC.

The comparative studies show that electrocatalytic activity increases gradually, as UH-CSMFC with urea fuel 0.5g/ml and its redox potential is higher in comparison to the urea liquid state UH-MFC with fuel in both the voltage polarities. The corresponding EIS measurement data, which matches the CV, trend fully. EIS measurements were performed to investigate the electrochemical behaviour of the compost soil. The high-frequency region in the semicircle shows the charge transfer resistance (R_{ct}) between the working electrode/electrolyte interfaces that is caused by the faradaic-redox reaction of the electrode. In the case of compost soil with urea fuel, R_{ct} is significantly decreased, which correlates with the increase electrocatalytic activity those results in a gradually reducing impedance.

The soil was known itself working as an electrocatalyst [4]. Similar to bacteria and enzymes, the soil may also catalyse the oxidation of urea. Due to the addition of the urea nitrogen source in the soil, the chemical reaction enhances the ph. The V_{max} for the high-affinity response of reaction ($N_2O \rightarrow NO \rightarrow N_2$) showed a relatively small peak, followed by first a decline peak and then a sharp increase. Urea is always a portion of food for the bacteria; urea stimulates bacteria to release urease [21, 26]. When urea is hydrolysed, it generates ammonia, transforms to ammonium ions (NH_3 to NH_4 ions) which are not going to volatilize. Following this, volatilization ammonification, by following the nitrogen cycle fixation lead to

nitrification and denitrification. Eventually release the last product to nitrogen (N_2) from UH-CSMFC through the process of nitrification and denitrification.

Electrochemical measurements of UH-CSMFC

Fig. 4(a) shows the strength of the fuel cell concentration from 0.1 g/ml urea to 0.5 g/ml urea sample. The highest catalytic activity observed at 14 hours with the inert Gr/Gr electrodes. Then, the device stability was checked by adding the 0.5 g/ml urea fuel at regular intervals of time. The power density was 18.26 mW/m^2, as evident from Fig. 4(b). Fig. 4(c) shows the effects of urea concentration on the power density of the cell [5, 29]. Electrocatalytic activity and electro-oxidation of urea showed the same trend for both the polarities of the redox potential. The urea fuel at higher concentration of 0.5 g/ml, a maximum oxidation peak generates power, and minimum over potential of the urea oxidation reaction was obtained. Thus, it was inferred that the current density was concentration-dependent, and the higher electrocatalytic activity was reported at the highest concentration of urea fuel. Which directly affects the power in compost soil performance**.**

The sustainability of the pH is confirmed at the beginning first running cycle (0 to 28 hrs) the pH compost was at lower 9.2 to slowly increase 9.7 in the fuel cell as compared with the liquid state UH-MFC while fuelling continually after every 28 hrs of the cycle in the Fig. 4(d).

The role of the pH is crucial at the liquid and the soil state of the compost fuel cell for the power output. Generally, microorganisms require the natural atmosphere for the optimal growth of the microbes for the generation of power. The biological and electrochemical reaction of the MFC changes with the pH level by consumption of urea. The new catalyst is cheap and used for cleaning process industrial wastewater, urea, and urine rich wastewaters with the generation of the energy from the waste products with UH-CSMFC.

When the fuel is feed at the beginning in the liquid state, the pH is near about 6.8 to 7.2 has a lower generation of electricity and still maintained the same Vs time for single cycle from 0 to 28 hrs with a single shot of fuel as shown form the Fig. 3(d). Yet, as compared urea fuel 0.5g/ml feed to the UH-CSMFC, this enhanced the power generation. The increase in the pH is due to the proton consumption and O.H. Generation by the anodic and cathodic side reactions, mostly indicating the effect of bacteria [7-9].

In fig. 5(a), (b), the power density reached its maximum peak at 14th hours and decrease to (0 to 28) hour's cycle. The I-V measurements study explains the sustainability of fuel cell, while the power generation the pH also shows the stable behaviour as we optimized for a long time vs hours the fuel supply continues. The sustainable study was shown in fig.5 (a). A commercial fuel cell has been refuelled several times after every 28 hours. Accordingly, the power generation was monitored to assess its sustainability. The results show that the stable functioning of the device continues until the fuel supplied to the UH-CSMFC fuel cell.

To study the consumption of urea, we performed I-V measurements in which urea fuel in the liquid state first was injected as fuel with regular interval of time, and its current density, power density is calculated. Initially, we have injected the urea fuel and left for the activation. The first sample was activated and shows maximum peak power at the 14 hours in the single cycle, and power decreases. After refuelling it in the 2nd cycle with fuel, power again repeated to its maximum. This indicates that the urea is consumed in compost MFC device to generate power [21].

In the performance of MFC device pH, sustainability is measured at room temperature until 140 hrs in comparison to the working of a fuel cell and check the sustainability of the UH-CSMFC. From the results, pH in the liquid state is decreased while in the power generation process in compost soil starts higher up taking fuel. The balanced system was established within the range of pH 9.2 – 9.7 in the compost-based system. The higher pH does not affect the electricity generation due to the buffer effects of the bacterial activities in the fuel cell [21, 27, 28]. The fig. 5(b) mentioned the pH difference between the liquid and soil state that the soil state has stable and higher pH, which is helpful for the electricity generation for the compost fuel cells optimized and monitored regularly. The consumption of urea is to be used for cleaning process industrial wastewater, urea, and urine rich wastewaters with the generation of the energy by UH-CSMFC.

Performance ofbacteria

To study the role of bacteria, enzymes for generating hydrogen and electric power. Compare the power of compost soil standard sample before, and after killing the bacteria by doing the autoclaved sterilization study at 120 ^{0}C, [29].

The compost, soil demonstrates, the role of bacteria, enzymes in the functioning of the MFCs, the compost soil containing cells were sterilized by autoclave treatment, and the power generated by these cells were compared with those that were not sterilized. While the first sample contained bacteria in the compost soil sample, the second sample that was autoclaved at 120^{0}C contained having no live bacteria. This was evident from fig. 6 (a) and 6(b), which shows the bacterial growth in plates after 28 hours. Bacterial colonies growth were visible in the plates, as shown in fig. 6(a), no colonies were found in the autoclaved sample shown in fig. 6(b). These results established the role of bacteria and enzymes in enhancing electricity production in the compost soil sample (fig. 6(c)). The Keithley I-V measurements studies shows that compost soil commercial device having a maximum power density of 18.26 mW/m^{2}; the maximum power density observed in the autoclave treated sample was only 0.03 mW/m^{2}. From these results, the role of microbes was demonstrated to be essential for the enhancement of power in the UH-CSMFC. In this compost soil system, MFC was found to produce enhanced energy and sustainability, due to the advantageous effects of different types of soil bacteria, enzymes (anaerobic and aerobic) [2, 21].

Mechanism discussion

An alkaline medium was used to carry out the urea electrolysis both for hydrogen production and direct electricity production:[5, 29]

The operating mechanism of UH-CSMFC is given below,

Anode reaction

The role of UH-CSMFC mechanism, as mentioned below.

$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$

$NH_3 + O_2 + 2e^- \rightarrow NH_2OH + H_2O$ ..... 1)

$NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4e^-$ ..... 2)

$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$

Cathode reaction

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

The overall reaction for anode and cathode

$2CO(NH_2)_2 + H_2O \rightarrow 3H_2 + N_2 + CO_2$

We have confirmed the combined mechanism for both compost soil, and urea fuel cell enhances the power generation due to urea fuel dissolved in a liquid state so that in soil bacteria, enzymes uptake, catalyze, then generate electricity and produce $H_2 + N_2 + CO_2$ mixed gas in UH-CSMFC [5, 7, 28, 29].

Compost soil in operation performs ammonification by the process of nitrification and denitrification process to reach to release the last product (N_2) as while supplying electron and protons. When urea was hydrolysed the urease enzyme releases in the soil is faster rate as compared to liquid, it generates ammonia, ammonium ions (NH_4 + ions) later. Following further, the ammonification and volatilization lead to nitrification and denitrification process.

Reaction 1 conversion urea to ammonia, then hydroxylamine, is catalysed by enzymes ammonia monooxygenase. Reaction 2 converts the hydroxylamine to nitrite, catalysed by the enzymes hydroxylamine oxidoreductase [22, 23].

Hydrogen is separated from a hydrogen/nitrogen/carbon dioxide mixture by an electrochemical separation method. The apparatus for separating hydrogen was similar to that used in a polymer electrolyte membrane fuel cell for producing an electrical current. Pure hydrogen gas can be separated without pressurization, and the separation rate can be easily controlled by the applied current [25].

Oxidation from urea to nitrogen gas, carbon dioxide, and hydrogen by bacteria results in the generation of ammonia or transform to ammonium ions, which are converted to carbonic acid C.O. $(OH)_2$, or carbamate as reported in the literature before. Ammonification leads to (*Nitrosomonas and Nitrobacter)* to NO_3 (nitrate) or directly NO_2 (nitrite) in a process called nitrification, which eventually produces nitrogen (N_2) [5, 21, 26, 28, 29,47-54].

Therefore, compost soil systems be a natural medium to transport electrons and protons easily in an eco-friendly and non-toxic manner for power and hydrogen generation. This study confirmed that the urea has a profound effect on the power and hydrogen generation from the UH-CSMFC. The focus is to get power from the UH-CSMFC in coming future by using waste like urea rich wastewater, urine, industrial wastewater, which contains much amount of urea and a huge source of hydrogen storage. [1-13,44-55].

Conclusions

The multifunctional role of UH-CSMFC was demonstrated. This UH-CSMFC was shown to generate power from using urea as fuel. Moreover, it can also lead to the production of hydrogen & electricity, reducing toxicity by consumption of urea from water pollution soil pollution, thus contributing to environmental clean-up. A 0.5 g/ml urea fuel concentration in the soil was found to be optimal, producing a power density of 18.26 mW/m^2. This device was shown to be sustainable for electricity generation. It was exploiting different types of energy-generating soil bacteria and enzymes already present in the soil. It can also remedy water, soil pollution. This study optimizes the advancement in the field of UH-CSMFC technology, by providing a sustainable, eco-friendly and cheap rate energy generation technology with plenty of scope of research in the future. On the other hand, for enhancing the power working on the stacks in series and parallel for enhancing the power in bulk systems.

Methods

Sample Preparation

Compost soil supplied by Seoul Seung Jin compost soil, Fertilisers Pvt Ltd., Korea. The compost is carbon-rich soil made from dry leaves and decomposed plant products. For both Graphite electrodes was used as anode and (cathode)**.** The initial studies were carried out with five different concentrations of urea fuel cell optimized from 0.1 g/ml, 0.2 g/ml, 0.3 g/ml, 0.4 g/ml, and 0.5 g/ml. For the comparison of power, the higher concentration of urea fuel was fixed at 0.5 g/ml in the liquid state mix with 50 grams of soil for a bulk fuel cell having surface area $15cm^2$. The dimension of the Urea-based fuel cell was designed with sustainable properties with optimized conditions used for Keithley (SMU-Model 2420) I-V measurements. For the catalytic activity of the urea fuel cell was performed first in small amount 3g of soil taken in $3.14cm^2$ area with the exact amount of urea fuel 0.5g/ml concentration fuel to study the coin cell with electrodes graphite foil for working and counter electrode for cyclic voltammetry studies,

later checked with the big size commercial design for catalytic activity and power density with UH-CSMFC.

Colony count study was done with standard nutrient broth to verify the effect of healthy growth of microbes on the samples at a urea concentration of 0.5 g/ml in the feed. Urea was first seeded into 9 ml peptone saline diluent (PSD) for two hours and incubated at fixed ambient temperature. The inoculated PSD was further diluted into fresh PSD 1:9, and diluted soil sample suspension (100 µL) was direct, distributed on the surface of the nutrient broth (N.B.) agar plates. After passing the (0 to 28 hours), the growth of bacteria was checked incubation at 37 ^{o}C.

Electrochemical characterization

For the I-V measurements, electrical characterization, Keithley high current source metre (SMU- Model-2420) interfaced with RS-232 mode, used to study the different I-V parameters. Cyclic Voltammetry is used just for checking the catalytic activity of the urea fuel cell studied by using the MPG-2, 16-channel battery system cycle, (Bio-Logic Scientific Instrument, France).

Declarations

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Authors' Contributions

VKM and HCJ finished the main work of this article, including deducing plotting the figures and drafting the manuscript. SJL, PDW, AHSR, and TWK provided useful suggestions. All authors read and approved the final manuscript.

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Availability of data and materials

All data are present in the manuscript.

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Figures

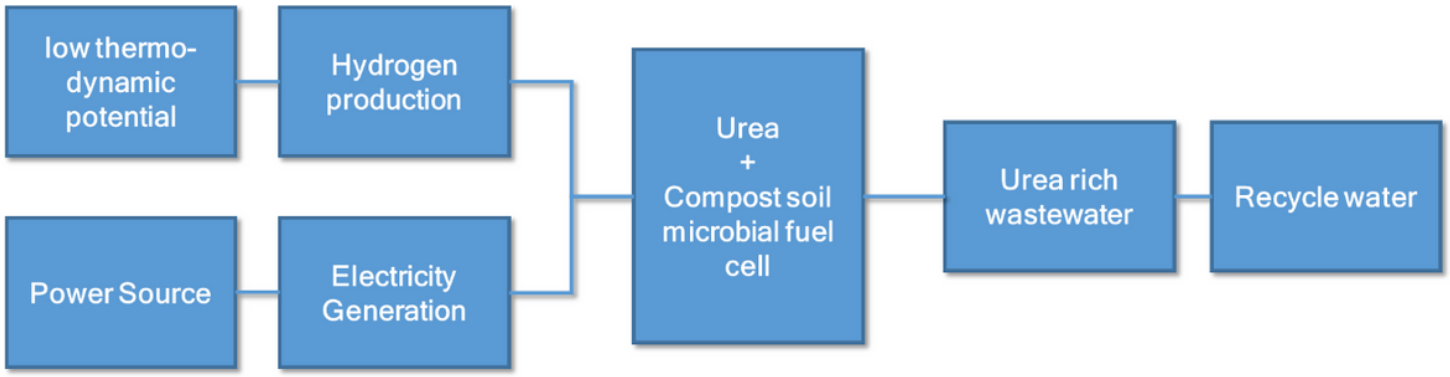

Figure 1

The multifunctional role of urea-hydrogen compost soil microbial fuel cell for urea fuel

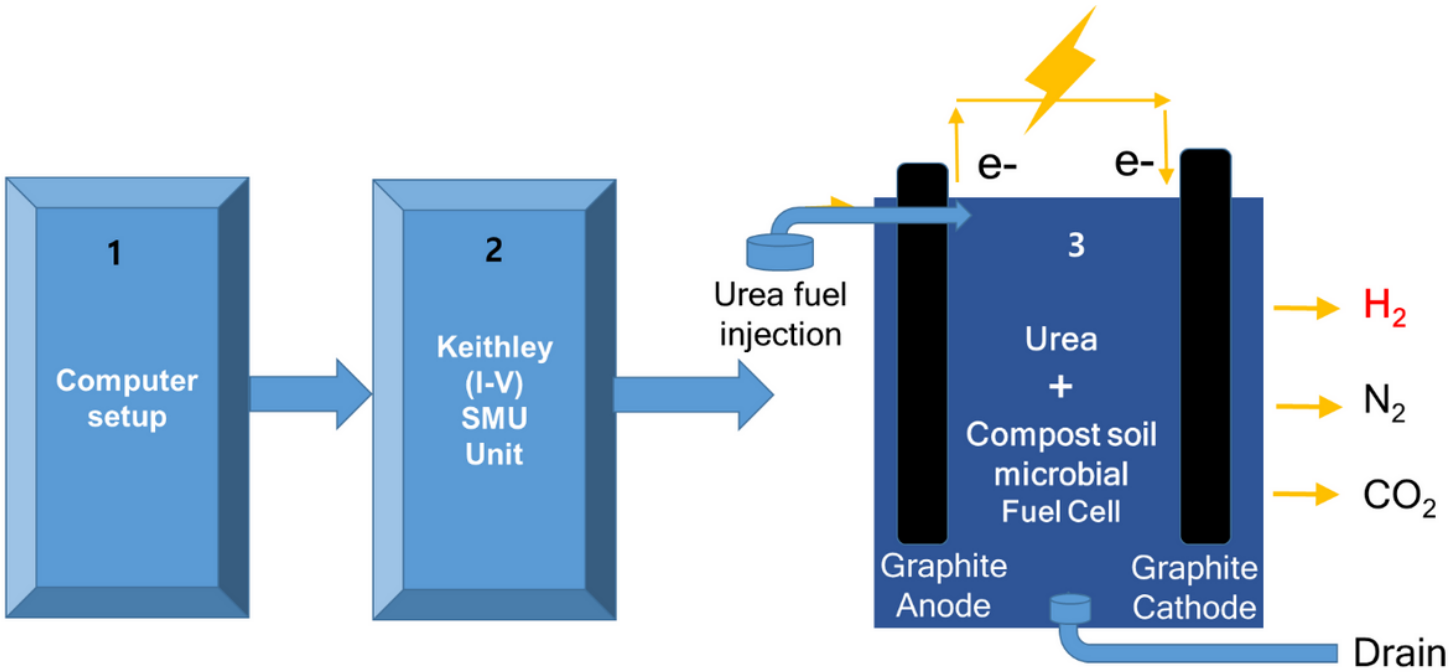

Figure 2

Schematic representations of the urea hydrogen compost soil microbial fuel cell for urea fuel

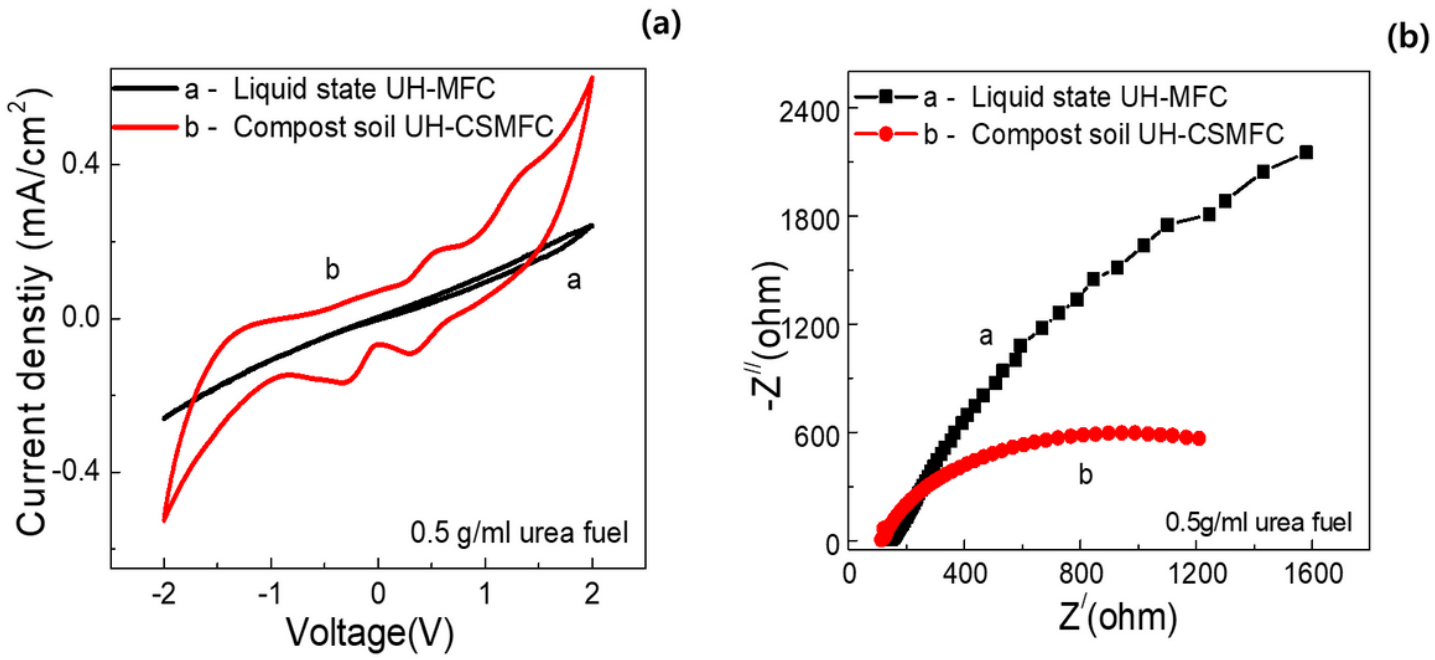

Figure 3

a) Showing the difference between liquid state UH-MFC(urea hydrogen microbial fuel cell) and compost soil based UH-CSMFC(urea-hydrogen compost soil microbial fuel cell), CV Studied comparsion liquid state vs compost soil fuel cell b) EIS studies

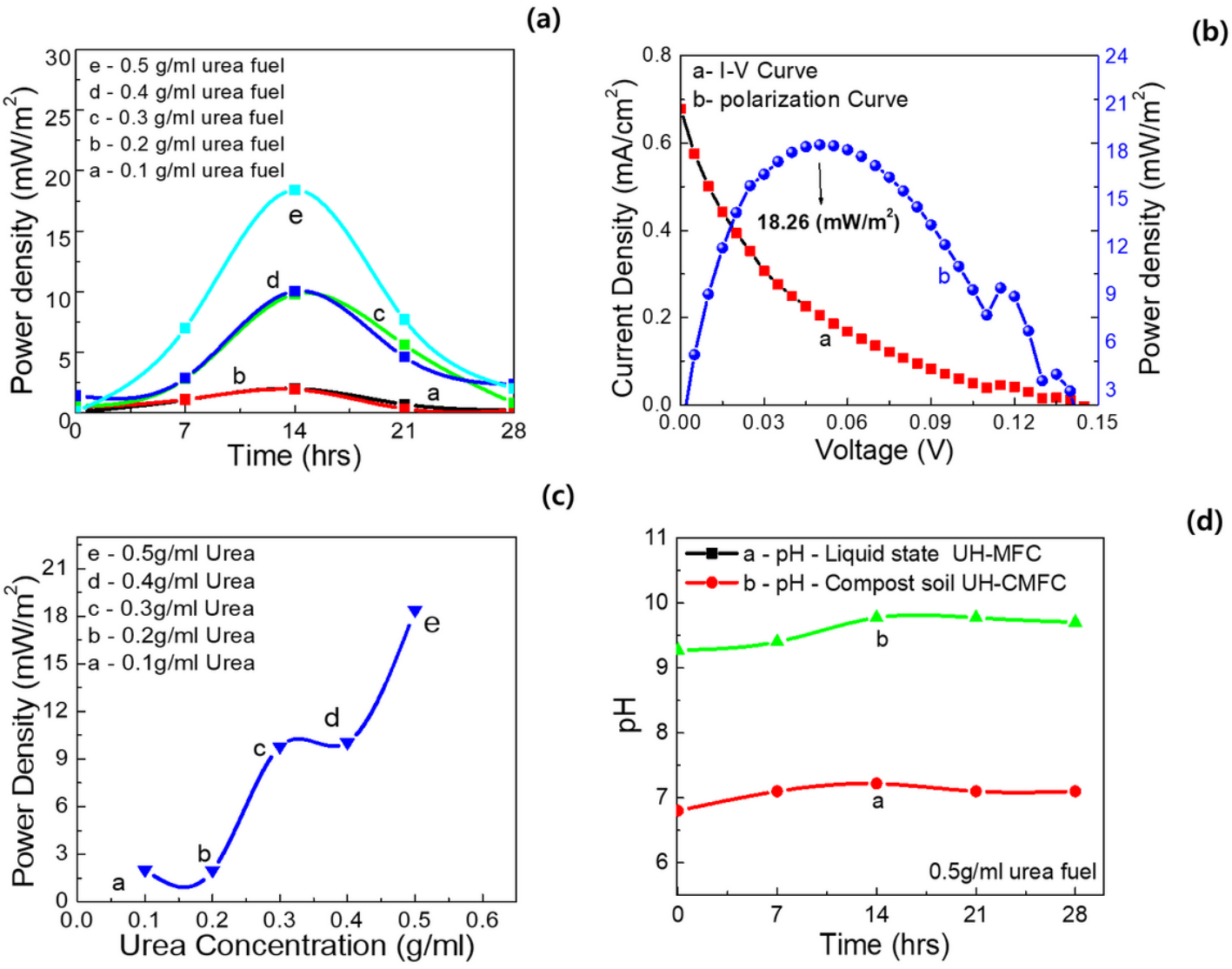

Figure 4

Keithley I-V measurment data with commercial device (a) (0.1g/ml to 0.5g/ml) concentrarion dependent catalytic activity Gr/Gr electrodes (a) Power density vs time of the UH-CSMFC (b) Polarization curve and I-V curve of device (c) concentration dependennt behaviour (d) pH difference on the liquid state UH-MFC and compost soil UH-CSMFC

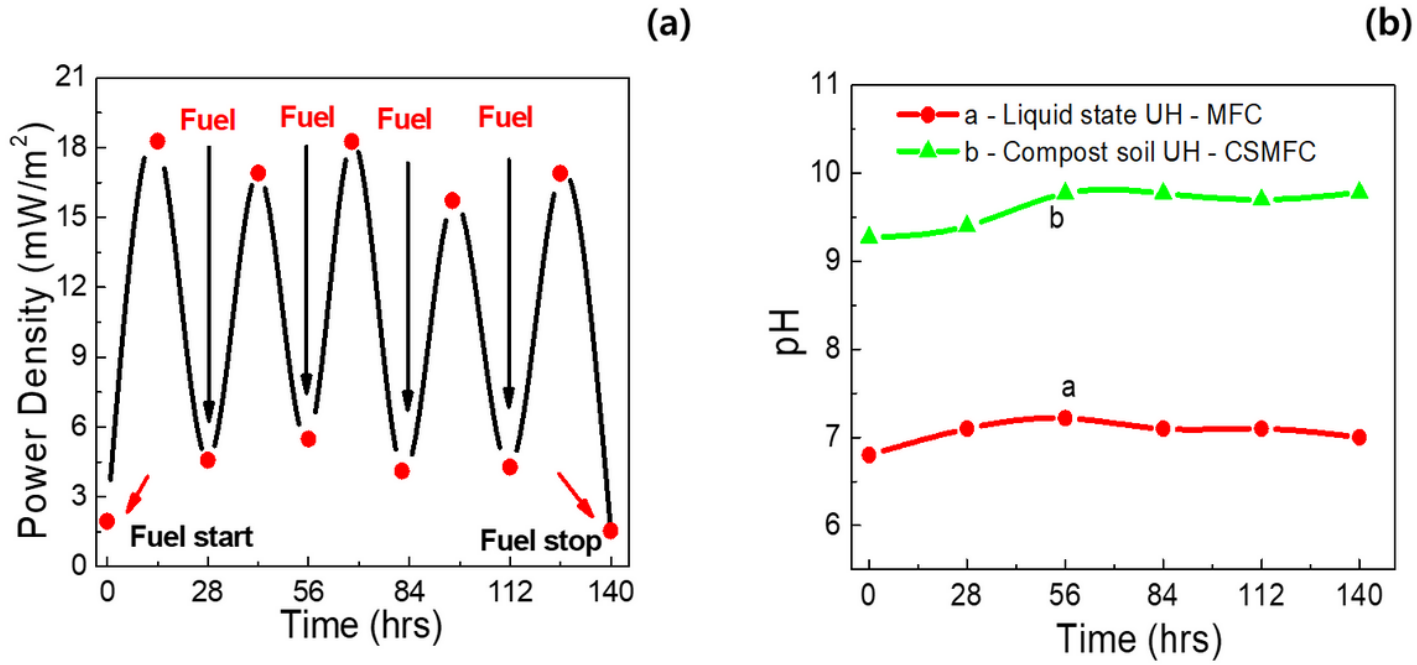

Figure 5

Sastainability study for 140 hrs.with urea fuel at 0.5gm/ml concentration fuel and pH sustainability for UH-CSMFC (a) UH-CSMFC sustainability study (b) pH sustainability study between liquid state UH-MFC and UH-CSMFC

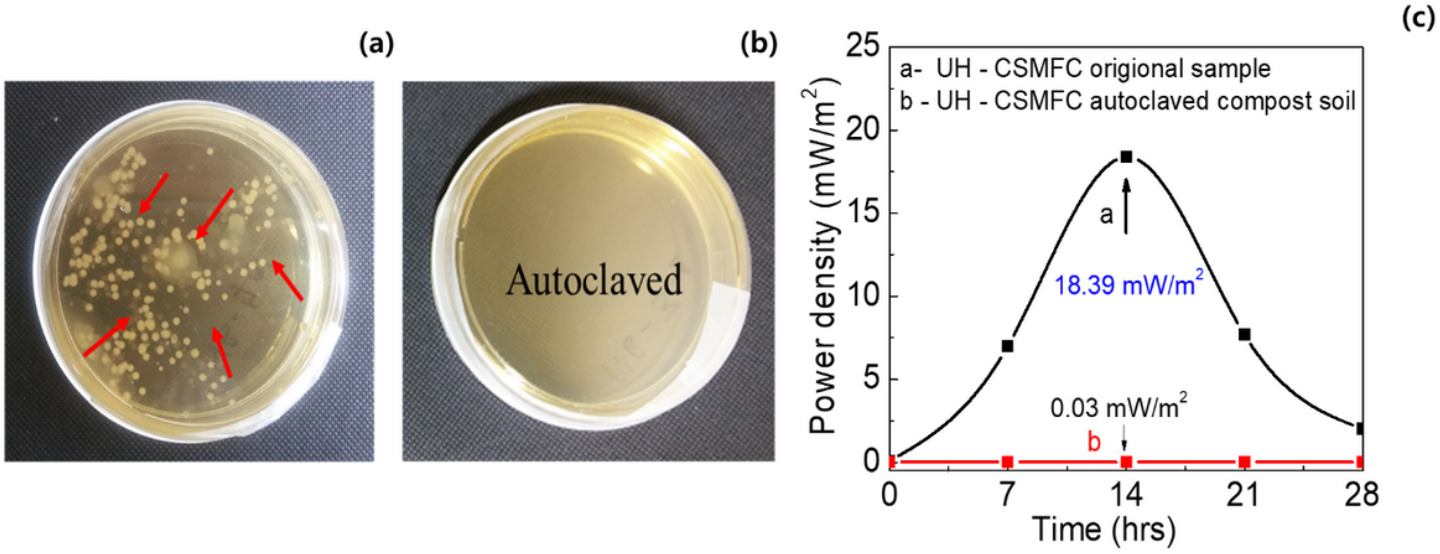

Figure 6

Effect of the bacterial study for compost soil UH-CSMFC (a) Growth of the bacterial colonies present (b) Growth of colonies absent (c) keithley I-V studies showing the effect of the bacteria.