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HIGH POWER AND ENERGY DENSITY OF REDOX ADDITIVE IN MICROBIAL FUEL CELL

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ABSTRACT
In the existing study, the performance of (I_2/I_3^-) as the efficient redox catholyte for escherchia coli based microbial fuel cell (MFC) was investigated and compared with conventional ferricyanide based system. This studies also examined the effect of applied current density, linear sweep voltammetry, open circuit voltage, discharge capacitance, Impedance, Energy and power density of the microbial fuel cell. Linear sweep voltammetry studies revealed the higher current density (3.3768 mAcm^{-2}) for(I_2/I_3^-)additive owing to its electro-reduction and this value is about 1.5 times higher in comparison to ferricyanide based system.The characteristics of (I_2/I_3^-)based MFC is attributed to its higher capacitive contribution, high conductivity, and high power, when compared to ferricyanide based MFC. The extreme power density of the MFC fabricated using (I_2/I_3^-)and ferricyanide additive at the measured current density of 50 μAcm^{-2}were observed to be 1,140 and 1,670.8303mWm^{-2}. Among the results, (I_2/I_3^-) basedMFCperformance displays excessive potential for enlightening the power generation of MFC.
Keywords: Biofuels, High Power Density, Microbial Fuel Cell, Redox additive, Regeneration.

INTRODUCTION
Development of alternative renewable energy systems has received much attention to encounter the world's growing energy demand owing to the tremendous rise in the world's population and faster fossil fuel depletion.Among the various next-generation energy storage devices, Microbial fuel cell (MFC) technology is not only the potential candidate for continual energy production, but also for wastewater management.[1-6] In contrast to the existing fuel cell technology, MFC uses the metabolic reaction of microorganisms as the anodic reaction through which the organic materials are converted into usable energy. In spite, of its technical demerits, such as poor current density and stringent reaction conditions, its environmentally benign status, an abundance of fuel sources and non-poisoning microbe metabolic process, made the MFC as the potential alternative energy source for power generation. However, the magnitude of power generation in MFC is far below, when compared to the existing fuel cell technologies, thus hindering its application aspects in certain power devices that require high energy output. Another serious limiting factor that restricts its application aspect is the production cost and its energy consuming process.
Achievement of full application potential of the MFC technology depends on various factors such as anolyte composition, electrodes, nature of microbes, separators and catholyte composition [7]. Significant research has been done on the influence of anolyte composition in MFC performance.[8-12] Alternatively, waste water obtained from various industrial sources has also been explored as the fuel source in MFC technology for electricity generation.[12-14] Recently, biomasses derived plants such as lignocellulose have been considered as a renewable carbon source for MFC applications.[15-17] Another important factor that significantly affects the MFC cell performance is the electrode. Several modified electrode systems that improve the voltage, power and current and thereby the efficiency of MFC has been studied.[18,19] For instance, Qiao et al. [18]stated that the performance of the MFC could be significantly improved on using nanostructured polyaniline

(PANI)/mesoporous TiO$_2$ composite as the anode in Escherichia colibacteria based MFC. The efficiency of MFC by varying the microorganisms has also been investigated by various researchers [22-24]. Generally, the bacteria used in the MFC cells do not act as a catalyst for electricity generation in the absence of a chemical catalyst such as platinum (Pt). On the contrary, Zhang et al.[21] claimed that E. coli based MFC produced the power density as high as 600 mWm^{-2}, corroborating that E.coli is sufficient enough to generate electricity, without the necessity of external chemical catalyst such as Pt. Qiao et al.[23, 24] reported that E.coli bacteria produced hydroquinone type endogenous compound that resulted in electrochemical redox behavior during fuel cell operations. The most influencing part of MFC is the ion selective separator, which separates the cathodic and anodic compartments preventing the water from anode to cathode and dissolved oxygen from the cathode to the anode. Though the nafion based proton exchange membranes have been used as ion selective separators in MFCs, significant research has been done on various other polymers and its nanocomposite systems to identify the potential cost-effective candidate to replace it [26-29]. Though the above-discussed parameters are considered to be limiting factor for the proper design of MFC, the key factor that hinders the cost-effective production of MFC with enhanced energy output is the cathode design, catholyte composition and the catalyst dealing with the oxidation-reduction reactions (ORR) in cathode compartment.[30] Research efforts have been made to overcome the issues such as high internal resistance, high cathodic potential and poor oxygen reduction rates[31-33]. In general, mediators with high redox potential have been used to lower cathodic potential in MFC[35-39]. Owing to its fast reduction kinetics and large redox potential, potassium ferricyanide(K$_3$[Fe(CN)$_6$]) has been commonly used mediator in MFC[34]. Alternatively, strong oxidizing agents such as potassium permanganate (KMnO4), hexavalent chromium (Cr^{6+}), hydrogen peroxide (H$_2$O$_2$) and ferrous ion activated persulfates (Fe^{2+}K$_2$S$_2$O8) have also been explored as potential mediators for MFC cells [36-39]. Recently, inducing electron transfer mechanism through external sources apart from electrochemical methods has received much attention due to its synergistic effect[39]. In this context, research is now focused on the development of daylight responsive photocathodes[40, 41]. Alternatively, Li et al.[42] reported solar light induced regenerable(I$_2$/I$_3^-$)cathodic electron acceptors (mediators) on the performance of the MFC cell performance using anaerobic sludge as the microbial source. However, to the best of our knowledge, no report is available on the effect of regenerative(I$_2$/I$_3^-$) cathodic electron acceptor on the E. coli based MFC cells. Though, (I$_2$/I$_3^-$) has several advantages such as solar light-driven regeneration capability and stability, its chemical reactivity towards endogenous hydroquinone compound generated by E.coli under fuel cell operation may hamper its electricity generating capability.

In the present work, E.coli based MFC cells have been fabricated using light responsive(I$_2$/I$_3^-$) as a cathodic electron acceptor and its electrochemical performances were compared with potassium ferricyanide based MFC system using linear sweep voltammetry (LSV), galvanostatic discharge (GLV) and electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

A dual-chamber H shaped MFC consisting of two glass compartments was used in this experiment (Fig.-1a). The glass compartments (50 mL) serving as anode and cathode chambers were parted by a proton exchange membrane (Nafion 117) and they are externally connected through Teflon bolts (Fig.-1a). Graphite rods with 8 mm diameter were used as the anode and cathode, respectively.

The bacterial strain (Escherichia coli K$_{12}$) was obtained from the department of microbiology, Vels University, Pallavaram. Aerobic growth of E. coli cells was carried out in sterilized Luria–Bertani (LB) medium (10 g/L glucose, 10 g/L peptone, 5 g/L yeast, 10 g/L NaCl, and pH=7), inoculated into the liquid medium and subsequently grew at 30□ in a constant temperature incubator for 24 hr[44,45]. Then the E. coli cells were maintained under anaerobic condition prior inoculating them into the MFC to pre-adapt bacterial metabolism in an anaerobic environment [45]. Subsequently, the E. coli cell was incubated for 24 h at 30□and the resultant cell suspension was used as the inoculating for the MFC experiments.

Nafion117 membrane, obtained from American Du Pont Company, Wilmington, USA was pretreated as discussed below prior using it for MFC fabrication. Nafion117 with diameter, 2.5cm was soaked in 3 % H$_2$O at 60°C for 1 h and subsequently washed with deionized hot water (80ºC) and dilute sulfuric acid (H$_2$SO$_4$; 0.5 mol/L). Then the treated membrane was washed with deionized, hot water two times and kept under deionized cold water.

The electrolyte for anode compartment (anolyte) was prepared by adding 2 g of E.Coli inoculated LB powder in 50 mL buffer solution (10 g/L Dipotassium hydrogen phosphate, K_2HPO_4 and 8.5 g/L potassium dihydrogen phosphate, (KH_2PO_4). Two different additives for the cathode compartment (catholyte) had been used in the present investigation as discussed below. Potassium ferricyanide ($K_3[Fe(CN)_6]$) based additive was prepared by adding 0.642 g of $K_3[Fe(CN)_6]$ (0.1 mol/L) to the 50 mL phosphate buffer solution (10 g/L Dipotassium hydrogen phosphate, K_2HPO_4 and 8.5 g/L potassium dihydrogen phosphate, (KH_2PO4). Alternatively, (I_2/I_3^-) based additive was prepared by dissolving 4.652 g potassium iodide (KI; 0.1 M) and 1.251 g of Iodine (I_2; 0.5 M) in 50 mL phosphate buffer solution. The fabricated MFC cells are referred to as MFC-F ($K_3[Fe(CN)_6]$) and MFC-I ((I_2/I_3^-) depending upon the additive used in the system. The electrochemical characteristics such as cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopic (EIS) measurements of the potassium ferricyanide and additives were performed using CHI 760D electrochemical work station (CHI instruments; Chenhua corp., Shangai, China) in the three electrode assembly with a Ag/AgClreference electrode. CV results of the $K_3[Fe(CN)_6]$) and (I_2/I_3^-)additives (in buffer medium) were obtained in the potential range of 0.00 to 0.6 V at the scan rate of 50mV s^{-1}. Linear sweep voltammetry (LSV) results of the additives were received in the potential range of -0.14 to 0.6V measured at the scan rate of 1.0 mV s^{-1}. Galvanostic discharge of the MFC cells (MFC-F & MFC-I) were determined using H-shaped two electrode assembly by varying current densities (10, 25, 50 and 100 µAcm^{-2}) using Neware battery tester (10 mA, 5V), Neware, China. Cyclic voltammetry (CV) and Electrochemical impedance spectroscopic (EIS) characterization of MFC two electrode assembly was done by CHI 760D electrochemical workstation (CHI instruments, Chenhua corp., Shangai, China).

During the galvanostatic discharge, a notable drop in open cell voltage (From OCV to lower value, Vm) is observed in both MFC-F and MFC-I cells. This potential drop (OCV-Vm) is attributed to ohmic resistance (V_{ohmic}) and it can be correlated to the equivalent series resistance (R_{ESR}) of the cells by equation (1).

$$R_{ESR} = V_{ohmic}/2 \tag{1}$$

Where R_{ESR} is equivalent series resistance, V_{ohmic}, is ohmic resistance and I is the constant current. During the galvanostatic discharge, the rate of decrement in cell voltage after the initial voltage drop is influenced by the capacitance of the MFC cell. The capacitance of the MFC cell was calculated from the slope of the galvanostatic discharge curve using the following relationship (equ.-2).

$$C_{MFC} = \frac{I_A}{dv/dt} \tag{2}$$

Where IA is the current density (applied current per unit area), dV/dt is the slope of the galvanostatic discharge curve.
Maximum power output (Pm) was determined for both the MFCs (MFC-F and MFC-I) by multiplying the maximum cell voltage (Vm) with current density (IA).

$$P_m = I_A/V_m \tag{3}$$

However, the above equation does not consider the observed capacitive decrement of the cell voltage during galvanostatic discharges and hence, the calculated Pm value may be higher than the actual power (power density) delivered by the cell at the applied current density.
The power density (PD) can be calculated from the energy delivered by the cell at the selected current density using the equation-4.

$$Energy\ density\ E_D = I_A \int_0^t V dt \tag{4}$$

Where t is the discharge time. The power density is obtained using the equation-5.

$$Power\ density\ P_D = E_D/t \tag{5}$$

RESULTS AND DISCUSSION

A photographic picture of MFC, was presented in the Fig.-1a, comprises two compartments namely anodic and cathodic, separated by a proton exchange membrane (PEM). In the MFC experiment, bacteria can metabolize organic substrate in the anodic chamber to produce electrons and protons, in which the electrons are moved to the surface of the anode, subsequently moving to the cathode through an external circuit,

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although the protons migrate to the cathode through PEM. Both electrons and protons are joined with the reduction of oxygen to water in the cathode chamber. Li.et al clearly explained the reaction mechanism of (I_2/I_3^-) system in Microbial fuel cell. Here we used normal daylight to regenerate the Iodide ions in the catholyte.

Further to understand the individual additive behavior as shown in the iodide ions are freely dissolved fundamental iodine by oxygen below the daylight, then the iodine syndicates with the iodide to form triiodide anion complex (I_3^-) [48]

Electrochemical Behavior of Redox Additives
To understand the role of potassium ferricyanide $(K_3[Fe(CN)_6])$ and (I_2/I_3^-) additives as cathode electron acceptor, the electrochemical characteristics such as cyclic voltammetry (CV), LSV and electrochemical impedance spectroscopy (EIS) were compared in standard three electrochemical cell consisting of glassy carbon, Ag/AgCl and platinum as working, reference and counter electrode respectively.

Figure-1b shows the CV results of potassium ferricyanide and (I_2/I_3^-) additives based three electrode assembly measured in the potential range of 0.0 to 0.6 V at the scan rate of 50 mV s^{-1}.Potassium ferricyanide additives based three electrode assembly shows both the redox potential between 0.20 to 0.33 V. Similar trend is noted in(I_2/I_3^-)additive system with a significant rise in redox peak current at around 0.48 V vs Ag/AgCl. In comparison to potassium ferricyanide additive based three electrode assembly, the relative rise in redox peak position and current as well as the increment in the loop area are corroborated to the higher redox potential, better ionic conductivity and larger areal capacitance induced by(I_2/I_3) additive on the glassy carbon surface. For instance, the areal capacitance value calculated using CV results is about 50 % higher for(I_2/I_3^-)additive (0.75 Fcm^{-2}),when compared to ferricyanide$(K_3[Fe(CN)_6])$ additive (0.5 Fcm^{-2}) based three electrode assembly confirming the above fact.

Linear sweep voltammetry results of MFC-I (0.1 M I_2+0.5 M KI additive) cells maintained at acidic (2N H_2SO_4, pH = 4), neutral (phosphate buffer, pH = 7) and alkaline (2N KOH, pH = 10) medium are shown in Fig.-1c. For comparison purpose, LSV result of MFC-F (0.1 M K_3[Fe (CN)$_6$]) maintained in neutral (phosphate buffer) medium is also included in Fig.-1c Relatively higher current densities over the range of potential are observed for MFC-I (maintained in neutral medium) in comparison to MFC-F (maintained in neutral medium). For instance, the current density of (I_2/I_3^-)additive (MFC-I) at 0.2 V is about 66.7 % higher in comparison to ferric ion additive (MFC-F) at the same voltage. Owing to higher redox potential (0.63 V) and electron transfer number (2e$^-$) of(I_2/I_3^-)additive, MFC-I exhibit better electroreduction mechanism in MFC-I in comparison to the potassium ferricyanide (0.43 V; e$^-$) additive based microbial fuel cell (MFC-F). These results are consistent with the result reported by Li et al.[42] To understand the effect of additive pH on the electroreduction mechanism of iodine ion based microbial fuel cell (MFC-I), the pH of the additive was adjusted by adding 2N sulfuric acid (H_2SO_4) (MFC-I-Acidic) and 2N potassium hydroxide solution (MFC-I-Alkaline). There is no notable variation in current density for both the MFCs (MFC-I-Acidic & MFC-I-Alkaline), when compared to MFC maintained in neutral medium (MFC-I-Neutral). For instance, the current densities of MFC-I-Acidic, MFC-I-Neutral and MFC-I-Alkaline are observed to be -2.95 mA cm^{-2}, -3.0 mA cm^{-2} and -3.1 mA cm^{-2} corroborating the fact that protons generated in acid or alkaline medium do not significant in the reduction of(I_2/I_3^-)ion and thereby revealing it as the stable cathode electron acceptor in MFCs[42].

Included in Fig.-1d is the typical Nyquist plots derived from electrochemical impedance spectroscopic (EIS) results of ferricyanide and (I_2/I_3^-)additive based three electrode systems measured in the frequency range of 10-2~105 Hz. As expected, the impedance spectrum of both systems consists of semi-circular arc followed by the straight line inclined at 45°C angle. Earlier proposed models reveal that the arc structure in high frequency zone consists of two semi-circles along with the inclined straight line. While the first semi-circle is corroborated to the catholyte solution resistance (R_S), the semicircle in the medium frequency zone is correlated to the charge-transfer resistance (Rct) on catholyte/glassy carbon interface, and the inclined straight line to the real axis correspond to the ion diffusion process within the glassy carbon surface [46].
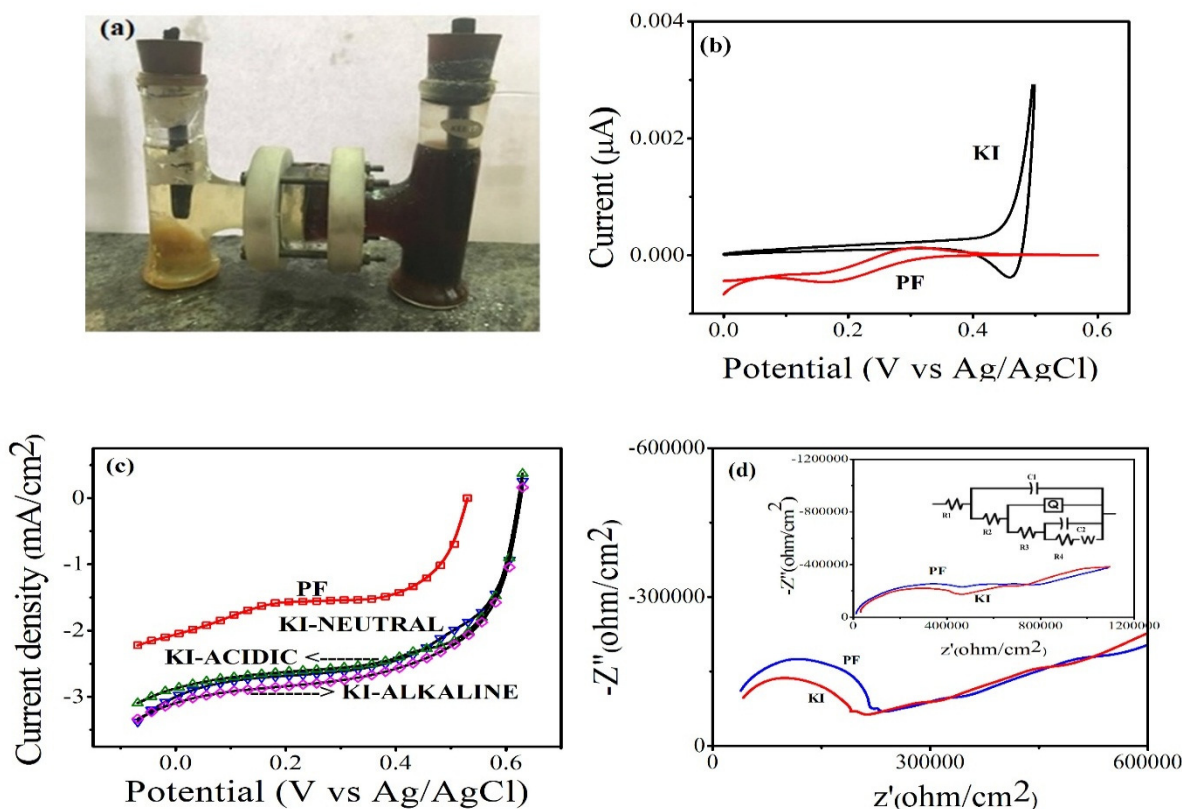
Fig.-1:(a) Photographic Picture of the Laboratory fabricated MFC (b) Cyclic Voltammetry of (I_2/I_3^-)at Scanning rate of 50 mV S^{-1}(c) Linear sweep voltammetry of twoadditives by varying different pH medium(acidic, alkaline, neutral) (d) Impedence Spectra of the Three and Two (inset) Electrode System: Comparison between MFC-F and MFC-I

As expected the catholyte solution resistance (R_S) is about 45 % lower for(I_2/I_3^-) in comparison to ferricyanide ($K_3[Fe(CN)_6]$) additive. Earlier report by Qian et al.[48] revealed that improved conductivity of(I_2/I_3^-)additive increases electron transfer rate and thereby reduction in ohmiclosses. The ionic conductivity of the both ferricyanide ($K_3[Fe(CN)_6]$) and (I_2/I_3^-) additive's were calculated from EIS results using the following equation:

$$K = (\delta/A) (1/R_S)$$
Where, δ/A is the cell constant (200 cm-1), R_S is the solution resistance.

The ionic conductivity of (I_2/I_3^-) additive (9.32 Scm^{-1}) is about 79 % higher, when compared to ferricyanide system ($K_3[Fe(CN)_6]$, 5.3 Scm^{-1}). Higher ionic conductivity for (I_2/I_3^-) additive is attributed to its higher electron transfer number (2e$^-$) in comparison to the ferricyanide ($K_3[Fe(CN)_6]$) additive(electron transfer number, 1e$^-$) [47], thus making it as a suitable additive for MFC cell fabrication.
Also, the charge transfer resistance (R_{ct}) between the catholyte and glassy carbon interface is 16 % lower for (I_2/I_3^-) ,when compared to $K_3[Fe(CN)_6]$ implying better charge transfer characteristics and thereby better electron transfer rate in the electrode/additive interface.
The variation in open circuit voltage (OCV) with respect to time of constructed two electrode microbial cells (MFC-F& MFC-I) are compared in Fig.-2a. Irrespective of the additive used, an exponential rise in OCV values is noted with respect to time for both of the cells (MFC-I & MFC-F). However, a noticeable rise in OCV value is observed for MFC-I (OCV 0.63 V)and this value is about ~19 % higher, when

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compared to MFC-F (OCV 0.53 V) cells. Similarly, the time taken to attain steady state OCV value is higher for MFC-I (4 days) in comparison to MFC-F cells (4 days). After attaining the steady state, OCV values remain constant upto1~2days of cell operation, after which a slight decrease in values are noted for both the MFC systems (MFC-I and MFC-F). Better OCV characteristic of MFC-I in comparison to MFC-F is attributed to the combined effect of its stability as well as redox potential of the respective catholyte. To corroborate this fact, volumetric titrations were carried out to calculate iodine (I^-) and ferric (Fe^{3+}) ion concentrations in the respective catholyte's of MFC-I and MFC-F after 5 days of cell operation. Titration studies indicated that relative concentration of ferric (Fe^{3+}) ion in MFC-F cell is 89 %, whereas iodine (I^-) ion concentration in MFC-I cell is 96 % after 5 days of cell operation. Relatively higher concentration of iodine ion in MFC-I revealed its stability, when compared to the ferric (Fe^{3+}) ion concentration in MFC-F. Also, the higher redox potential (0.63 mV) of iodine catholyte (I^-/I_3^-) in comparison to ferric ion ($K_3[Fe(CN)_6]$, 0.43 mV) corroborates that it is a promising candidate as the catholyte for microbial fuel cells.
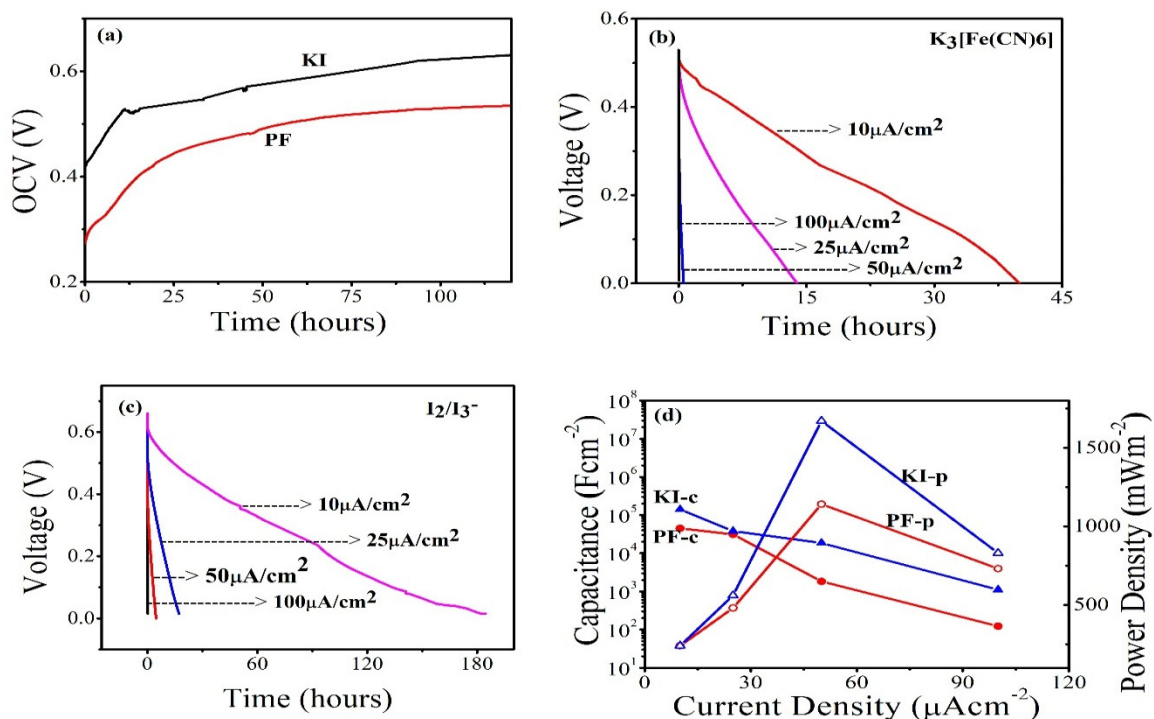

Fig.-2: (a) Open circuit variation for ferricyanide and Iodine/Iodide (b) Galvanostatic discharge curves of MFC-F and (c) MFC-I discharge with different applied current density (d) Areal capacitance values versus applied current density of MFC-F and MFC-I. Power density vs current density curve demonstrate the performance of the two additives in MFC.

Galvanostatic discharge characteristics measured at various current densities of the redox catholyte based two electrode microbial fuel cells (MFC-F& MFC-I) are included in Fig.-2b and c. Both MFC-F and MFC-I shows an initial voltage drop (V_{ohmic}) that are corroborated to the internal resistances in the cells. Interestingly, internal resistance is lower for potassium ferricyanide catholyte based microbial fuel cell (MFC-F), when compared to iodine catholyte based MFC (MFC-I) at the measured current densities. For example, voltage drop (V_{ohmic}) is about 1.7 % for MFC-F, whereas it is about 6.94 % for MFC-I at the current density of 10 μAcm^{-2}. Thus, the equivalent series resistance (R_{ESR}) calculated using equation (1) is observed to be higher for I_3^- based MFC (MFC-I) in comparison to ferricyanide based MFC (MFC-F) in the measured current densities (Fig.-3a).

According to Zhang [48], internal resistance or otherwise R_{ESR} is the summation of resistances induced due to reaction kinetics (R_{act}), ohmic resistance (R_{ohmic}) and mass transport (R_{conc})

$$R_{ESR} = R_{act} + R_{ohmic} + R_{conc} \tag{6}$$

Though, the ohmic resistance induced by solution resistance (R_S) and charge transfer resistances (R_{ct}) calculated for I_3^- catholyte using three electrode assembly is relatively lower, when compared to ferricyanide catholyte, higher R_{ESR} for the former (I_3^-) may be attributed to the relative increment in resistances due to variation in reaction kinetics (R_{act}) as well as its mass transport (R_{conc}) in comparison to the $K_3[Fe(CN)_6]$ system. To reveal this fact, EIS characterization of MFC two electrode assemblies (MFC-F & MFC-I) were done and the typical Nyquist plots are included in Fig.-1d (inset). As anticipated, relatively large semi-circular arc and small linear portion is observed in both the MFC's (MFC-F & MFC-I) confirming the slower electron transfer process in both the system. For evaluating the obtained EIS data, the components in the MFC were fitted using the equivalent circuit model consisting of charge transfer resistances of anode and cathode (R_1 & R_3), additive resistance including proton exchange membrane (PEM), anolyte and catholyte (R_2), capacitance with constant phase element (C_1 & C_3) and diffusion elements (R_4 and C_4) (Fig.-1d (inset)) [50]. In comparison to ferricyanide catholyte based MFC (MFC-F), a significant rise in anodic charge transfer resistance (R1; 128 %), additive resistance (R2; 167 %), diffusion resistance (R4; 22 %) is observed for iodine/iodide catholyte based MFC (MFC-I), whereas notable drop in cathodic charge transfer resistance (R_3; 62.7 %) is detected for the same. Higher value of R_1, R_2 and R_3 corroborates to the higher internal resistances for MFC-I in comparison to MFC-F system, which could be attributed to the resistances induced due to variation in reaction kinetics as well as mass transport in the system. Earlier report by Zhang et al. revealed that e.coli bacteria generates endogenous hydroquinone compound under fuel cell operation. There is strong possibility that the generated the hydroquinone compound can react with both ferricyanide ($K_3[Fe(CN)_6]$) and iodine/iodide (I_3^-) catholytes under fuel cell operation and thereby alters the reaction kinetics as well as the mass transport. Jiang et al[50] revealed that ferric ion (Fe^{3+}) reacts readily with hydroquinone (HQ) leading to the formation of semiquinone (Q^*) radicals and ferrous ion, which is subsequently oxidize back to ferric ion (Fe^{3+}) as shown in the equation (12):

$$HQ + Fe^{3+} \rightarrow Q^* + Fe^{2+} \rightarrow HQ + Fe^{3+} \tag{7}$$

Alternatively, Kolthoff [48] reported that reaction between the hydroquinone and iodide ion is a reversible reaction leading to the formation of quinone as shown in the equation-8.

$$HQ + I_2 \leftrightarrow Q + 2I^- + 2H^+ \tag{8}$$

As per the report, the potential of HQ/Q system is equivalent to I_2/I^- system in its equilibrium state [51], which is subsequently depend on H^+ concentration in the medium. In contrast to ferric ion catholyte, variation in reaction kinetics as well as its mass transport of (I_2/I_3^-) ions plays a vital role in maintaining the equilibrium state, which subsequently alters the internal resistance in the system.

After the initial voltage drop, both the MFC system (MFC-F & MFC-I) displays progressive decrease in voltage with respect to time irrespective of external current densities (Fig.-2b and c).However, the time taken for complete discharge is significantly higher for MFC-I, when compared to MFC-F. For instance, At the measured current density of 10 μAcm^{-2}, MFC-F took approximately 3 hrs for complete discharge, whereas MFC-I takes about 17 hrs. As expected, time taken for completely discharge decreases with increasing current density for both the MFC systems. Significant improvement in discharge characteristics for MFC-I system can be correlated to its supercapacitive performance, when compared MFC-F system. The areal capacitance was calculated using the discharge profile and the equation (2) and the results are shown in Fig.-2d. In comparison to MFC-F, the areal capacitance is relatively higher in the measured current densities corroborating higher charge storage capability in MFC-I. For instance, the areal capacitance is about1, 41043.7235 Fcm^{-2} higher for MFC-I, when compared to MFC-F. Significant rise in capacitive contribution is responsible for higher electricity generation in MFC-I system. This fact is well supported by the power density of MFC's calculated using the equations (5).

Power density increases linearly with the external current densities for both the MFC system (MFC-F and MFC-I). However, the increment in power density is relatively higher for MFC-I, when compared to MFC-F at the measured current density (Fig.-2d). For instance, the power densities of the MFC's measured at the external load of 50 μAcm^{-2} are 1,140 (MFC-F) and 1,670mW cm^{-2} (MFC-I) corroborating the positive

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contribution of (I_2/I_3^-) catholyte in electricity generation. From these results, we can conclude that iodine/iodide catholyte is the better catholyte for *escherchia coli* based MFCs.
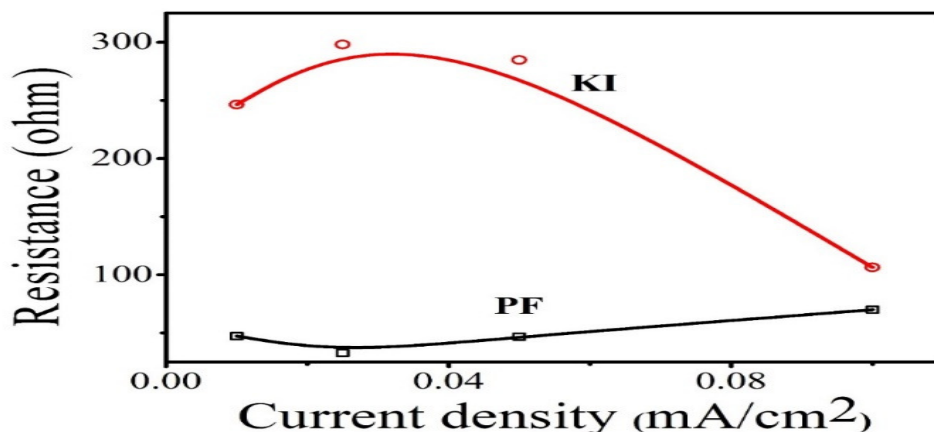

Fig.-3: Difference of the internal resistance with respect to different current density.

CONCLUSION

In this study, we have demonstrated the (I_2/I_3^-) additive is the effective cathode electron acceptor for escherichia coli based MFC in comparison to ferricyanide $(K_3[Fe(CN)_6]$ based system. From LSV experiments, it has been concluded that (I_2/I_3^-) system yielded relatively higher power and energy in the selected potential range, when compared ferricyanide based MFC. Significant rise in discharge time is noted for I_3^- additive based MFC revealing its higher performance. Inspite of higher internal resistance, better capacitive contribution of I_3^- additiveresulted in slight improvement of power density and it can be improve by adding additives or mediators to boost power density in future. So thereby electricity generation capability for I_3^- based MFC in comparison to ferricyanide based microbial fuel cell.

ACKNOWLEDGEMENT

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