A One-compartment direct glucose alkaline fuel cell with methyl viologen as electron mediator

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HIGHLIGHTS

- A glucose–air alkaline fuel cell without using noble metal catalysts has been developed.
- The rudimentary fuel cell generates a maximum power density of 0.62 mW m\textsuperscript{-2}.
- The high performance is attributed to the use of MV and nickel foam.
- Main oxidation products are small organic acids indicating deep oxidation of glucose.

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ABSTRACT

Glucose is abundant, renewable, non-toxic and convenient as a fuel for fuel cells, but current technologies are unavailable for us to directly oxidize it to obtain energy. Fuel cells using enzymes and microorganisms as catalysts are limited by their extremely low power output and rather short durability. Fuel cells using precious metal catalyst are expensive for large-scale use. In this work, a one-compartment direct glucose alkaline fuel cell has been developed that use methyl viologen (MV) as electron mediator and nickel foam as the anode. The rudimentary fuel cell generates a maximum power density of 0.62 mW cm\textsuperscript{-2}, while the maximum current density is 5.03 mA cm\textsuperscript{-2}. Electro-catalytic activities of MV and the nickel foam in alkaline conditions were studied by cyclic voltammetry. It is indicated that the high performance of the fuel cell is attributed to the combined use of MV and nickel foam. \textsuperscript{13}C-NMR and HPLC were used to analyze oxidation products of glucose. The result shows that the principal oxidation products are short-chain organic acids indicating deep oxidation of glucose is achieved.

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1. Introduction

Over the past decades, studies on the modern use of biomass have increased rapidly [1–6]. The use of biomass is gradually becoming a viable approach to reducing our reliance on fossil fuels. However, imaginative ways to convert these materials into useful, electrical energy are still required. Glucose is one of the most abundant sugars in nature and can be derived from a large amount of waste biomass that is generated by agricultural activities and from dedicated energy crops. Now, the commonly used approaches to derive energy from glucose include production of ethanol and conversion to hydrogen, but these approaches are hindered by technical and economic problems [7–12]. An alternative approach to derive energy from glucose is to feed it into a fuel cell and extract energy from its oxidation to generate electricity. In this case, the chemical energy can be directly converted into electrical energy with less energy loss.

Extensive efforts have been made to study glucose as fuel for direct fuel cell, enzymatic fuel cell and microbial fuel cell (MFC). Oxidizing glucose to gluconic acid with enzyme has been explored for powering implanted medical devices [13]. In this kind of fuel cell, the most critical technical hurdle is its extremely low performance. Furthermore, it’s difficult to keep the activity of enzyme and the stability of power output [14–16]. In MFCs, bacteria are used to generate electricity from the oxidation of glucose with acetic acid or carbon dioxide as the end products. MFCs have relatively long-term durability and complete oxidation of glucose can yield 24 electrons [17,18]. However, the performance of microbial glucose fuel cells is also extremely low; the state-of-the-art power density is 0.431 mW cm\textsuperscript{-2} at a voltage of 0.664 V [19].

Alternatively, direct glucose fuel cells in which metal catalysts catalyze the oxidation of the sugar have been developed [20–23]. They provide distinct advantages over other forms of fuel cells,
such as high performance and easy-of-operation. General direct glucose fuel cells often use noble metal catalysts such as platinum to liberate electrons from glucose [20,21]. The noble metal cata-
lysts are expensive for large-scale use, meanwhile the conversion rates are low and the reaction temperature is high. Although there are a small number of studies which use non-precious metals as catalysts in direct fuel cell [22,23], but several factors limit their applicability, including (i) low transformation efficiency as glucose is only oxidized to gluconolactone and (ii) low catalytic stability caused by poisoning effect of high concentration of hydroxyl ions and reaction intermediates.

Viologens, derivatives of 4, 4'-bipyridine, play an important role as electron relays in systems in which electron transfer is initiated by photochemical or electrochemical processes [24]. The viologens exist in three main oxidation states, namely $V^2- \rightarrow V^+ \rightarrow V^2$. These redox reactions, especially the first one ($V^2+ \rightarrow V^+)$, are highly reversible and can be cycled many times without significant side reactions. Because of these desirable characteristics, viologen derivatives have been extensively investigated [25–27]. Methyl viologen (MV), which is one of the world’s most widely used herbicides, has long been used as redox mediator in MFCs to facilitate the electron transfer from microbial cells to the current-collection electrode [26,27]. However, there are few studies on using MV in non-noble metal catalyzed alkaline fuel cells, and there are still different views on its catalytic mechanism [23,28].

In this study, a glucose–air fuel cell has been developed using MV as electron mediator and nickel foam as anode current collector. The fuel cell was optimized in terms of various operating conditions. Cyclic Voltammetry (CV), Nuclear Magnetic Resonance (NMR) and High Performance Liquid Chromatography (HPLC) techniques were used to study the kinetics of the glucose oxidation reaction and identify the intermediates and final products. The overall goal of this work is to develop a less expensive and high-performance glucose fuel cell system and to explore the catalytic mechanism of MV.

2. Experimental section

2.1. Materials

Methyl viologen (MV) was purchased from J&K Scientific Ltd (China). Carbon cloth (HCP330), 60% by weight PTFE solution (DupontPTFE 60 wt.% dispersion in water), 10% by weight platinum on carbon powder (10% Pt on Vulcan XC-72), 5% by weight Nafion® solution (DupontNafion® perfluorinated ion-exchange resin) were all purchased from Heshen, Inc. (Shanghai, China), carbon black powder (Cabot Vulcan XC-72) was purchased from Cabot Co., Ltd. (Tianjin, China). Chemical reference standards for HPLC were purchased from Sigma–Aldrich. Iso-propanol, KOH and α-glucose were all of analytical grade. All solutions were prepared using deionized water.

2.2. Air-breathing oxygen-reduction cathode assembly [29]

Carbon cloth was first soaked in 6 ml 40% PTFE solution and then air-dried. After that, it was sintered in a furnace at 370 °C for 20 min and then cooled to room temperature. Repeated processes above were taken until weight change reached 30%. Let carbon black to spread well in 40% PTFE solution. One side of the carbon cloth was coated with this carbon suspension and air-dried, then sintered and cooled. Well shaken 60% PTFE solution was applied to the previously coated side of the carbon cloth. The carbon cloth was air-dried, sintered and cooled. Repeated steps above were taken for more than three times to obtain a total amount of 4 PTFE coatings. The catalyst ink was prepared by mixing Pt/C catalyst with a loading of 0.5 mg Pt/cm², iso-propanol as the solvent and 5 wt% Nafion® as the binder. Well dispersed catalyst ink was brushed on the side opposite the diffusion layer coatings. The homemade cathode was air-dried for 24 h before use.

2.3. Fuel cell apparatus and assembly

The one-chamber fuel cell is made from polymethyl methacrylate (PMMA). As can be seen in Fig. 1, the fuel cell was composed of an anode, an air-breathing carbon cloth cathode and a 30 mm diameter cylindrical internal chamber. A teflon-coated stir bar anchored on a wire was used to stir the chamber solution when necessary. The anode substrate was nickel foam (purity: 99.9%, number of pores per inch: 110, density: 380 g/m², average pore size:590 μm, thickness: 1.7 mm) from HANBO (Shenzhen) Co. Ltd. Nickel wire was used for electrode connection because it is corrosion-resistant and inexpensive. Both the anode and cathode had an exposed area of 3.80 cm². A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire as a counter electrode. Solution of glucose, MV, and KOH was injected anaerobically into the compartment, and dissolved oxygen was removed from the solution by purging nitrogen gas for 10 min. All of the experiments were conducted at room temperature and ambient pressure. Multimeter (VICTOR 8145B, Shanghai, China) was used to monitor the open circuit voltage change of fuel cell. Cyclic Voltammetry (CV) was conducted by using a Corrtest CS-120 model electrochemical workstation (Wuhan, China). Electrocatalytic properties of MV for glucose oxidation were measured in a half-cell consisting of a platinum wire or nickel wire as working electrode, an SCE as reference and a platinum wire as counter electrode. Character the nickel-foam anode was performed in a same configuration, except for the working electrodes were replaced by nickel foam with the same weight about 0.30 g.

2.4. Product identification

NMR and HPLC were used to identify the products of glucose oxidation. Natural abundance α-glucose was used in 13C-NMR (Varian INOVA 500 MHz NMR Spectrometer). For comparison purpose, two kinds of experiment were conducted: (1) electrolyte was placed in a test vial exposed to the open air without electrode and the oxidation products were identified after two days; (2) electrolyte was placed in the fuel cell to produce electricity and the oxidation products were identified after the extraction of the electricity. Electrolyte solution was dehydrated by vacuum freeze-drying and redissolved in D2O. The HPLC system (Shimadzu LC-10AVP) was equipped with a UV–Vis detector (Shimadzu SPD-10A VP), and an Aminex HPX-87H column (Bio-Rad, 300 x 7.8 mm), using 4 mM H2SO4 as eluent at a flow rate of 0.6 ml/min at 35 °C. Identification of the products was achieved by comparing their retention time to those of the corresponding standards.

3. Results

3.1. Effect of KOH concentration

The effect of the KOH concentration on cell performance at fixed glucose and MV concentrations of 1 M and 5 mM is presented in Fig. 2. The data shows that the cell performance increased with increasing the concentration of KOH. The polarization curve showed the maximum current densities are 0.08, 0.31, 1.19 and 2.94 mA cm⁻² for 0.01, 0.1, 1 and 3 M KOH, respectively. The peak power density with 3 M KOH was 0.46 mW cm⁻², which was significantly higher than others. This result indicates the significant
Fig. 1. Photograph (a) and schematic structure (b) of the one-compartment direct glucose alkaline fuel cell.

Fig. 2. Polarization curves and power profile for different concentration of KOH with 1 M glucose in 5 mM MV solutions.

Fig. 3. Polarization curves and power profile for different concentration of glucose in 5 mM MV and 3 M KOH solutions.
3.2. Effect of glucose concentration

Fig. 3 depicts three polarization and power density curves showing the dependence of fuel cell performance on the concentration of glucose. The glucose concentration was changed from 0.3 M to 1 M in 5 mM MV and 3 M KOH solution. The maximum power and current monotonically increase with the glucose concentration. When the glucose concentration ranges from 0.3 M to 1 M, the maximum power increases from 0.24 to 0.46 mW cm\(^{-2}\) and the maximum current increases from 1.14 to 2.94 mA cm\(^{-2}\). OCV of the fuel cell decreases when the glucose concentration decreases with the same concentrations of MV and KOH. This result shows the performance of alkaline glucose fuel cell upgrades with the increase in glucose concentration from 0.3 to 1 M.

3.3. Effect of MV concentration

The cell performance with different MV concentrations at 3 M KOH and 1 M glucose is shown in Fig. 4. The cell performance monotonically increases with MV concentration from 0 to 15 mM. The limiting current density increases from 1 to 5.03 mA cm\(^{-2}\) and the power density increases from 0.11 to 0.62 mW cm\(^{-2}\). The fuel cell performance increases almost 6 times.

3.4. Electrocatalytic property of MV for glucose oxidation in alkaline condition

In order to study the anodic oxidation behavior of glucose catalyzed by MV in alkaline media, Cyclic Voltammetry (CV) in the region of −1.1 ~ 0.4 V vs. SCE (saturated calomel electrode) was used to characterize the anodic oxidation process. In 1 M KOH, the glucose oxidation occurs at −0.7, −0.35 and 0.2 V respectively (Fig. 5). In 3 M KOH, the nickel wire shows little catalytic ability for glucose oxidation, but the difference on anodic peak current can be dramatically reduced by adding of 5 mM MV (Fig. 6). It indicates that MV plays a critical role in improving the electrochemical oxidation of glucose on a nickel electrode in 3 M KOH solution.

Fig. 7 shows the replacement of nickel wire by nickel foam can dramatically increase the anodic peak current by two orders (from 0.0003 A/cm\(^{-2}\) to 0.03 A/cm\(^{-2}\)). The high cell performance should be due to high surface area of porous nickel foam.

OCV almost doesn't change (625 mV–644 mV) when the concentration of MV changes, but OCV of the experiment without MV (510 mV) is obviously lower than others. The result suggests that MV concentration plays a critical role in improving fuel cell performance.
3.5. Effect of scan rate of cyclic voltammetry on the glucose oxidation in the fuel cell

Fig. 8a shows the CV response of the nickel anode in a fuel cell with 1 M glucose, 3 M KOH and 5 mM MV at different scan rates (from inner to outer): 60, 70, 80, 90, and 100 mV s\(^{-1}\). It indicates that the anodic peak currents increase with the increase of scan rates. Fig. 8b reveals that the first oxidation peak current is proportional to the square root of scan rates, indicating that the electrochemical oxidation of glucose in the anode is diffusion-limited. The linear regression equation is \(i = 0.00262 V_{1/2} + 0.02517\) with a correlation coefficient of \(r^2 = 0.9993\).

3.6. Product Identification from glucose oxidation

Fig. 9a shows the natural abundance \(^{13}\)C-NMR spectrum following glucose oxidation, which was operated at room temperature. MV appears three peaks which locate at 48, 126 and 146 ppm respectively. The existence of formate peak (171 ppm) on the spectrum indicates that MV can catalyze reactions that break carbon–carbon bonds of glucose. Significant amounts of unreacted glucose are seen, indicating that the oxidation process can hardly use up all the substrate. A controlled experiment in which glucose oxidation was operated under the same conditions (minus MV) did not show the appearance of formate, indicating that MV is very important for carbon–carbon bonds breaking reactions.

Fig. 9b is a natural abundance \(^{13}\)C-NMR spectrum of glucose from the fuel cell which operates under the same conditions as above. It shows a similar spectrum with Fig. 9a, indicating formate and gluconate are the major products of glucose oxidation.

Unlabeled \(^{13}\)C-NMR has the problem of weak intensity. In order to look further for the presence of reaction intermediates and other reaction products, samples were taken from the fuel cell and examined by HPLC. The result is shown in Fig. 10. The figure shows the existence of oxalic acid (peak 2), glucuronic acid or glucaric acid (peak 3), gluconic acid (peak 4), glyceric acid (peak 5), formic acid (peak 8) and acetic acid (peak 9), indicating that most of the oxidation products are small-molecule acids under the experimental conditions.

4. Discussion

Viologens (1,1’-dialkyl-4,4’-bipyridinium, \(V^{2+}\)) are known to undergo one-electron reduction to produce the cation radical (\(V^{+}\)), which is easily oxidized to \(V^{2+}\). Our study indicates \(V^{2+}\) can dramatically improve the performance of the direct glucose fuel cell. It allows use of non-precious metal—nickel as electrode material under strong alkaline conditions, which are beneficial for glucose oxidation. By employing MV as electron mediator and nickel foam as the anode electrode, the maximum power density obtained was 0.62 mW cm\(^{-2}\) and the maximum current density of 5.03 mA cm\(^{-2}\) can be achieved.

The reaction schemes for glucose oxidation in alkaline solution with MV as electron mediator in a direct fuel cell are as follows:

![Image](image_url)
On the anode:

\[ 2\text{MV}^{+} \rightarrow 2\text{MV}^{2+} + 2e^{-} \quad (1) \]

On the cathode:

\[ \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^{-} \rightarrow 2\text{OH}^{-} \quad (2) \]

In the solution:

\[ \text{Glucose} + 24\text{MV}^{2+} + 24\text{OH}^{-} \rightarrow 6\text{CO}_2 + 18\text{H}_2\text{O} + 24\text{MV}^{+} \quad (3) \]

Overall:

\[ \text{Glucose} + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} \quad (4) \]

The complete oxidation of glucose to carbon dioxide and water is associated with the transfer of 24 electrons to MV$^{2+}$ per molecule of glucose, as described by the reaction in Eq. (3). However, our study results have confirmed that glucose is not completely oxidized in our experimental conditions. The theoretical maximum rate of electron transfer from glucose oxidation has been seldom reported in abiotically catalyzed glucose fuel cells. Instead, glucose is principally oxidized to gluconolactone (or gluconic acid), which transfers only a single pair of electrons. Our study shows that MV is capable of catalyzing reactions which oxidize gluconolactone further, and oxalic acid (resulting from 22-electron-transfer processes) and other short-chain organic acids have been detected in our systems using HPLC.

Polarization curves of a fuel cell with MV as electron mediator are approximately straight lines (Fig. 2–4), exhibiting a rather low activation polarization loss. The middle parts of the polarization lines are ohmic region which demonstrates the linearity of current versus load resistance. Slope of the line reflects the apparent resistance of the cell. It can be seen from Fig. 4 that slopes of the polarization curves decrease when the MV concentration increase, indicating that MV accelerates the electron transfer rate so that the resistance of the cell is reduced and the amount of reduced MV available for the current generation is increased. The same phenomenon can also be seen in Fig. 2 that the slope of the polarization curve decreases when the KOH concentration increases, indicating that the increase of KOH concentration can also reduce the resistance of the cell. The higher KOH concentration not only increase electrolyte conductivity, but also supplies more OH$^{-}$ ions that are needed for the oxidation reaction in the solution (Eq. 3). In summary, the anode current produced from glucose oxidation is greatly dependent upon the concentrations of glucose, KOH and MV in the chamber. The concentration of any of them increases will bring an improvement of the cell performance.

It is reported that nickel has the catalytic ability for glucose oxidation in alkaline solution, which mainly originate from the Ni (II)/Ni (III) redox couple [30]. The cyclic voltammetry of glucose at a nickel electrode at low KOH concentration is reflective of the three distinct areas which is similar to that of a platinum electrode [31]. Three oxidation peaks are observed in the anodic sweep. The oxidation mechanism associated with each potential region of the nickel electrode involves three steps. The first step is the chemisorption...
and dehydrogenation of the glucose molecule at the hemiacetalic carbon 1 atom (C1) [32]. The second step is the oxidation of the chemisorbed glucose catalyzed by the adsorbed hydroxide. The third step is the glucose molecules are oxidized at high potentials parallel to the oxidation of Ni (II) to Ni (III) species [33]. However, the anode potential range in our alkaline fuel cell is between $0.9 \text{ V}$ and $0.1 \text{ V}$, so Ni (III) does not exist in this experimental condition and the glucose oxidation by step three might be negligible. In the high concentration of KOH, the current density of the nickel anode decreases sharply. The explanation for this phenomenon is as follows. For a given anode, the potential depends on the local concentrations of both glucose and hydroxyl ions. On one hand, a higher KOH concentration can enhance the glucose oxidation reaction kinetics [33], but on the other hand, too high KOH concentration leads to an excessive coverage of hydroxyl ions that decreases the number of sites available for glucose absorption and this inhibits the catalytic ability of nickel and causes the overall rate of glucose oxidation to decline [34].

MV dissolved in deaerated solution can be reduced by glucose under the condition of relatively high concentration of KOH. MV$^2+$ is colorless and MV$^+$ is deeply blue, so the formation of MV$^+$ can be visualized from the blue coloration of the solution. When only MV was dissolved in the water, the solution was colorless, but when glucose, KOH and MV were mixed together in the cell chamber, the solution turned blue at once, indicating that the MV$^2+$ was reduced to MV$^+$ immediately. The redox couple MV$^2+/MV^+$ has a low potential, suitable to act as electron-transfer mediator on the nickel anode. In this process, electrons are released from glucose molecules, then MV$^2+$ captures electrons and turns to MV$^+$. MV$^+$ transfers the electrons to the nickel anode and is oxidized back to MV$^2+$, so that there is no net consumption of the MV species. The electrons reach the cathode through the external circuit and are captured by oxygen. When the oxygen is reduced on the cathode, the whole reaction is complete. Fig. 11 shows the proposed reaction mechanism in our fuel cell.

Glucose is a polyhydroxy aldehyde, and is unstable in alkaline medium. Wheeler et al. [35] indicated the major oxidation products of glucose were formate and carbonate. This news is exciting, because all the carbon–carbon bonds are broken. Glucose could release more electrons and more power can be gotten from glucose complete oxidation. Our results of $^{13}$C-NMR and HPLC analysis confirmed that there is carbon bond breaking in the glucose molecule and the principal oxidation products are small organic acids, including formic acid. However, carbonate was not found in the glucose oxidation products, which is not consistent of Wheeler’s result. It may due to different reaction conditions were used in this study. It is reported glucose transformation in alkaline medium involves the following reactions: enolization/isomerization, $\beta$-OH elimination, $\alpha$-dicarbonyl cleavage and (retro-) aldolization et al. [36,37]. HPLC results allow the modeling of the proposed reaction pathway as presented in Fig. 12. $\alpha$-glucose can be partially oxidized into gluconic acid, glucuronic acid and glucaric acid. Enediol anion species are involved in both isomerization and decomposition reactions. $\alpha$-fructose comes from the isomerization of $\alpha$-glucose.

Fig. 12. Proposed oxidation pathway of glucose in the direct alkaline fuel cell.
Aldehydes such as glyceraldehyde can be obtained by retro-aldol condensation of D-fructose. Further oxidation of the aldehydes produces organic acids, such as formic and acetic acids.

The performance of the fuel cell is affected by many factors [23], such as the efficiency of the cathode, mass transfer efficiency in the compartment. The good physical and chemical properties of nickel foam also make the cell more powerful. Our results show that the combined use of MV and nickel foam can enhance the cell performance significantly, which make it possible to use inexpensive material as an electrode substrate in alkaline fuel cells. Our air-breathing cathode is homemade, there is still room for improvement of its efficiency and the power can be improved based on this.

As a widely used broad-spectrum herbicide, MV is toxic and its heavy usage may bring an environmental problem. In order to reduce its environmental impact, MV can be immobilized on the anode surface or harmless alternatives with similar performance should be found to replace MV. Further researches about reaction mechanism are necessary to be held to provide more insight on the rate-limiting step so that we can get better use of the glucose oxidation to harvest electricity power.

5. Conclusion

A glucose-air alkaline fuel cell without using noble metal catalysts has been developed and tested. The resulting current and power density is higher than most of the existing glucose fuel cell designs, such as enzymatic fuel cells and MFCs. The fuel cell is simple to assemble and operate with a variety of inexpensive and abundant materials. It is shown that the concentration of MV, glucose and KOH can significantly influence the cell performance. Electrochemical oxidation of glucose in the fuel cell is diffusion-limited. The $^{13}$C-NMR verified that there is carbon bond breaking in the glucose molecule. Main glucose oxidation products in this fuel cell are short-chain organic acid, such as oxalic acid, formic acid and acetic acid. It should be also mentioned that although the fuel cell system developed in this work is promising in term of its higher performance with cheaper anode electrode than all other reported glucose fuel cells, some other issues, such as deep and complete oxidation of glucose merit extensive research.

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