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Mechanistic understanding of monosaccharide-air flow battery electrochemistry

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ABSTRACT

Recently, an inexpensive monosaccharide-air flow battery configuration has been demonstrated to utilize a strong base and a mediator redox dye to harness electrical power from the partial oxidation of glucose. Here the mechanistic understanding of glucose oxidation in this unique glucose–air power source is further explored by acid–base titration experiments, ^{13}C NMR, and comparison of results from chemically different redox mediators (indigo carmine vs. methyl viologen) and sugars (fructose vs. glucose) via studies using electrochemical techniques. Titration results indicate that gluconic acid is the main product of the cell reaction, as supported by evidence in the ^{13}C NMR spectra. Using indigo carmine as the mediator dye and fructose as the energy source, an abiotic cell configuration generates a power density of 1.66 mW cm^{-2}, which is greater than that produced from glucose under similar conditions (*ca.* 1.28 mW cm^{-2}). A faster transition from fructose into the ene-diol intermediate than from glucose likely contributed to this difference in power density.

1. Introduction

As the environmental, social and economic costs of traditional energy sources increase, the search for alternative energy sources continues to gain momentum. As various sources of energy are examined and models proposed, fuel cell technologies are emerging as one of the most efficient methods for energy harvesting that convert chemical energy into electricity. Discussions around fuel cells are almost exclusively concentrated on hydrogen or simple alcohol types in proton-conducting membrane-based configurations [1] with some mentioning of solid oxide fuel cells using hydrocarbons [2]. Unfortunately, most of these fuel cells predominately depend on expensive precious metal catalysts and still lack a low cost fuel from natural resources.

A fuel cell/flow battery capable of directly harvesting electricity from a naturally abundant high-energy source would provide great promise in the search for alternative energy. Such high-energy sources of fuel could easily include carbohydrates. Simple monosaccharide sugars such as glucose or fructose are readily available and natural. Tapping into these energy resources would be considered environmentally friendly and renewable. Although it is a concern to use food crops also as fuels, there are substantial merits to pursue this pathway, and we believe potential solutions to minimize or even avoid such conflict can be found. A live example is that Brazil remains active in the pursuit of conversion of sucrose to ethanol for its transportation needs. Although studies do show that the fermentation of corn sugar to produce ethanol results in a net gain in consumable energy [3], the process is energy intensive and ethanol combustion is still subject to the constraint of the Carnot cycle, resulting in a significant loss in the utilization of the chemical energy to produce useful work. Effective and direct conversion of the same chemical energy to electric power by carbohydrate electrochemical cells promises better efficiency than those via the fermentation and combustion pathway [3].

Previous attempts to harness power from glucose, in the form of a fuel cell, have predominantly been in the form of bio-fuel cells that utilize biological catalysts [4–7] or microorganisms [8–10]. These biotic approaches have additional benefits in application and fuel sources that merit continued research. Nonetheless, these approaches continue to battle with limited power output and lifetime. Abiotic pursuits in carbohydrate fuel cell designs have been hampered by the inability of the precious metal-based catalysts to sustain power production due to poisoning or fouling [11,12].

Recently two abiotic fuel cell designs have been presented using inexpensive chemical dyes as mediators in alkaline solutions capable of harnessing electrical power from various carbohydrates [13,14]. In the approach reported by Wheeler et al. [14], the mediator dye is considered as a catalyst and a complete oxidation of glucose to CO_2 to harness 24 electrons is suggested in their elevated temperature cell with Nafion separator. In contrast, the

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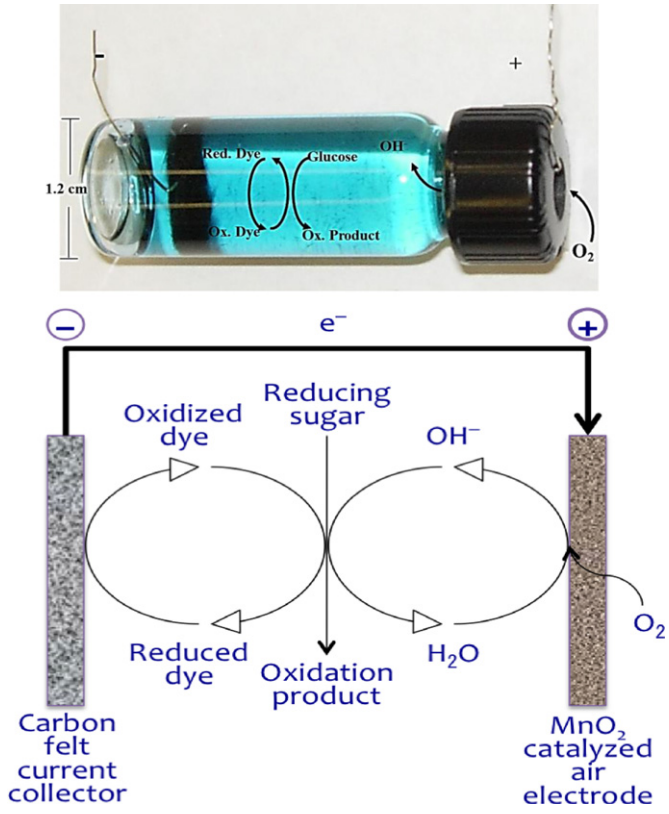


Fig. 1. An illustration and schematic of a monosaccharide-air flow battery cell made in our labs. Cells are made from simple containers that can seal an air-breathing cathode and keep it in contact with the reaction solution. No membrane is used, and there are no precious metals in the anode or cathode. The schematic explains the reactions involved in the cell chemistry.

abiotic cell reported by us, as shown in Fig. 1 [13], operates at room temperature and does not require the use of separator. The mediator merely acts as a charge transfer medium and does not act as a catalyst. A two-electron redox pathway is suggested as the cell reaction that produces power. In conjunction with a commercially available air-breathing electrode, both approaches can generate a considerable amount of power, as high as 3.8 mW cm^{-2} in some of our trials.

Our previous report [13] included preliminary data that seemed to suggest a limited coulombic efficiency under high rates in long time trials, as evidenced by the fact that only ~30% of the available electrons were harnessed. This percentage was derived based on an assumption of a 2-electron oxidation of glucose according to a proposed mechanism suggested in literature [15–17]. To understand what limits the coulombic efficiency and how to improve it, further insight into the power producing mechanism and any parasitic side reactions is needed. Therefore, in this work, better mechanistic understanding of such reactions are explored using acid–base titrations, ^{13}C NMR, UV/VIS and by using an alternative carbohydrate, fructose, and an alternative mediator, indigo carmine (IC). This is also the first report of fructose and IC being used in our abiotic cells. IC is also a FDA approved food dye, making it a safe alternative to the previously used methyl viologen also known as paraquat.

Simple acid–base titrations provide evidence of end products from the glucose oxidation as well as the resulting OH^- concentration in the solution. These titrations, in the absence of one of the components to produce power, can help indicate the source of parasitic power loss to side reactions. ^{13}C NMR data can help identify reaction products. Comparing power production from fructose, in contrast to its chemical isomer glucose, helps substantiate the mechanism of the reaction. It is also possible to monitor the UV spectra of the carbohydrate and NaOH reaction to compare rates of intermediate formation. IC is a mediator dye whose redox potential is dependent on pH [18]. This property is different from that of methyl viologen previously used in our experiments, whose redox potential is independent of pH. This difference allows further understanding into the power production dependence on the dye redox potential. Additionally, comparisons between power production with glucose and fructose with different mediator dyes further reveal the reaction step that is affected by different sugars and dyes.

2. Experimental

2.1. Materials and preparations

Indigo carmine (IC), NaOH, glucose, and fructose were purchased from Sigma–Aldrich and were used without further purification. Carbon felt (product number 43199) with a thickness of 3.18 mm was purchased from Alfa Aesar. An air-breathing oxygen-reduction cathode with an MnO_2 catalyst was purchased from Electric Fuel and used from the package without treatment.

An in house flow battery cell apparatus was made as described previously [13]. The electrolyte is composed of NaOH, glucose or fructose, and mediator dye with a variation in concentration of each component.

2.2. Techniques and methods

2.2.1. Acid–base titrations

All titrations were performed with 1 M hydrochloric acid and 15 mL samples at room temperature. Samples contained 3 M NaOH, 1 M glucose and 10 mM indigo carmine except when otherwise specified. A Microlab interface was used to monitor pH change and volume added during titrations.

2.2.2. ^{13}C NMR

^{13}C NMR spectra were obtained from a facility at the University of Hawaii – Manoa. Samples of the electrolyte solution were taken every hour starting from 0 h, quick frozen with liquid nitrogen and stored at −80 °C during sample transfer.

A Bio-logic VMP3 potentiostat/galvanostat was used to conduct all electrochemical measurements. In the cell, the air-breathing cathode material was exposed to the open air without any additional airflow or oxygen enrichment.

3. Results and discussion

3.1. State of reducing sugar oxidation and origin of CO_2

It has been reported [14] that the oxidation of glucose via a method similar to the one presented here produces the ultimate breakdown of glucose to CO_2. However, we have not seen convincing evidence that CO_2 is a product from glucose oxidation in the abiotic cell configured in our labs. It would be very valuable if all the 24 electrons from the oxidation of glucose to CO_2 were available to such abiotic cells for electrochemical power generation so the full potential of the energy content in the carbohydrate can be harnessed. It is therefore critical to verify if complete oxidation of reducing sugar such as glucose indeed occurs in the cell. Getting a better understanding of this process could help us improve the design of the harnessing apparatus to make such high energy harvesting possible.

To further investigate the reaction products and to determine side-reaction products and rates, acid–base titrations of samples that contained either OH^- or OH^- and IC were compared with samples of solutions that contain these components with glucose. It was

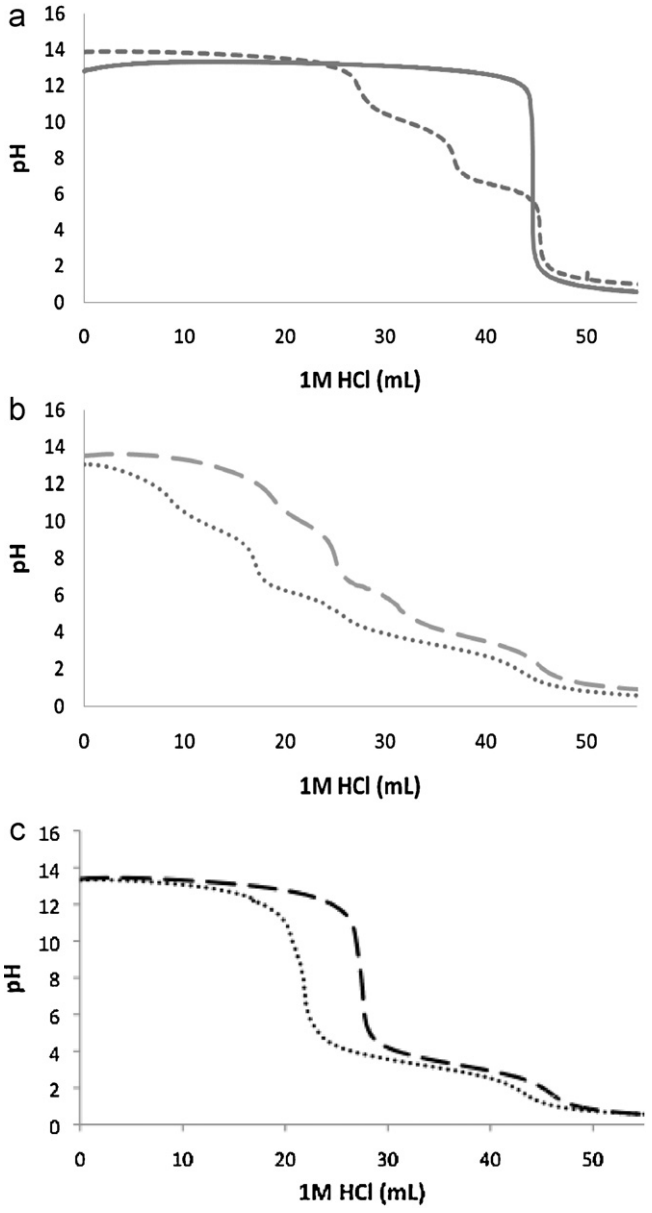


Fig. 2. (a) Titration of a sample of OH^- (solid line) compared to that of a sample of OH^- that has been stirred for two days open to the air (dashed line). (b) The results of titrations of a sample of OH^- and glucose (dashed line) compared to a sample of OH^-, glucose and indigo carmine (dotted line). Both of these samples were also stirred open to the air. (c) A sample of OH^- and glucose (dashed line) compared to a sample of OH^-, glucose and indigo carmine (dotted line). These reactions were under a nitrogen atmosphere with a cathode collecting electrons from the reduced dye. As shown, there is no indication from titration that there is any CO_2 in the form of the carbonate or bicarbonate ions in solution when the CO_2 from the atmosphere is excluded.

noticed that the products of the reactions are the same when the sample is stirred vigorously under an O_2 atmosphere (a chemical pathway) or when the sample was allowed to transfer electrons to a carbon felt anode poised at a potential of 144 mV by the mentioned cathode material (an electrochemical pathway). In both cases, the ultimate electron acceptor is O_2, as expected in the glucose oxidation.

The ultimate concentration of OH^- in solution corresponds to the first sigmoidal titration dip on acquired titration plots, as shown in Fig. 2. This is consistent with OH^- being the strong base in these samples. The next two drops in the titration curves correspond to the formation of carbonate and bicarbonate ions with pK_as of 10.3 and 6.4, respectively. The final protonated product from this series of reactions has a pK_a of *ca.* 3.7. This is consistent with what would be expected from gluconolactone, which, when protonated, becomes gluconic acid.

Fig. 2(a) shows a titration curve of a sample OH^- solution (solid line) compared to that of a OH^- solution that has been stirred for two days open to the air (dashed line). The amount of the OH^- (3 M) dissolved in the sample (15 mL) is equal to about 45 mL of 1 M HCl titrated, as clearly indicated by the solid line with a fresh solution. It is known that CO_2 could dissolve in alkaline solution, as experienced in alkaline fuel cells and metal–air batteries. As expected, the stirred OH^- sample solution traps CO_2 from the air as carbonate and bicarbonate ions. The quantity of the trapped carbonate and bicarbonate ions is equivalent to the amount of OH^- lost, as indicated by the same terminal point at about 45 mL of HCl that has been added to the samples in the titration. ^{13}C NMR data of such stirred samples also confirms the presence of carbonate and bicarbonate ions.

Fig. 2(b) shows the results of titrations of a sample of OH^- and glucose solution (dotted line) and a sample of OH^-, glucose and IC solution (dashed line). Both samples were also stirred open to the air. When glucose is present in the alkaline solution (dotted line) a chemical species with a pK_a of 3.7 appears, which was not observed previously in samples shown in Fig. 2(a). When IC is added, the amount of the chemical species with a pK_a of 3.7 increases (dashed line). This observation suggests the concentration of this chemical species (pK_a = 3.7) is increased by the presence of the dye. The presence of this chemical species with pK_a of 3.7 is consistent with the hypothesis that glucose is deprotonated to produce an intermediate, resulting in the formation of gluconolactone or gluconic acid. It also supports the proposed mechanism, that the mediator dye serves as the medium of removing electrons from the intermediate to form gluconolactone. The presence of the dye alters the equilibrium among the species involved in the reaction according to Le Chatelier's Principle. It also indicates, however, that even in the absence of the dye there is a side reaction that oxidizes the glucose in the formation of the species with a pK_a of 3.7, which does not lead to the production of power as evidenced by previous experiments [13]. This simple acid–base titration experiment confirms the presence of a chemical pathway for the cell reaction to produce gluconic acid as a result of glucose partial oxidation in the alkaline solution. The presence of the mediator dye alters the equilibrium of this reaction.

The observation of the species present with a pK_a of 3.7 is likely due to the fact that the concentration of hydroxide and glucose are significantly higher than that of IC. Thus, the concentration of ene-diol intermediate formed at any given time is likely much higher than the concentration of IC. The strong basic environment apparently drives the formation of gluconic acid from the intermediate even in the absence of IC. Because the chemical conversion of glucose to gluconic acid without IC reduces the amount of electrons available to the IC, power production could be improved by identifying a more soluble redox dye.

When the reaction occurs in a nitrogen atmosphere, as shown in Fig. 2(c), there is no indication from titration that there is any CO_2 in the form of the carbonate or bicarbonate ions in solution. This is also the result when the atmosphere is 100% oxygen or when the sample is simply not stirred and in its early stage without side reaction. The ^{13}C NMR of samples that are stirred under nitrogen atmosphere or simply not stirred is also consistent with the assumption that there is no appreciable amount of carbonates in these samples. Fig. 3 shows ^{13}C NMR data (a) before cell operation and (b) after 11 h of cell operation. The peak around 185 ppm is consistent with that of gluconic acid. Its magnitude also correlates with a peak around 22 ppm, whereas the corresponding chemical species has yet to be identified. The peak at 22 ppm is relatively

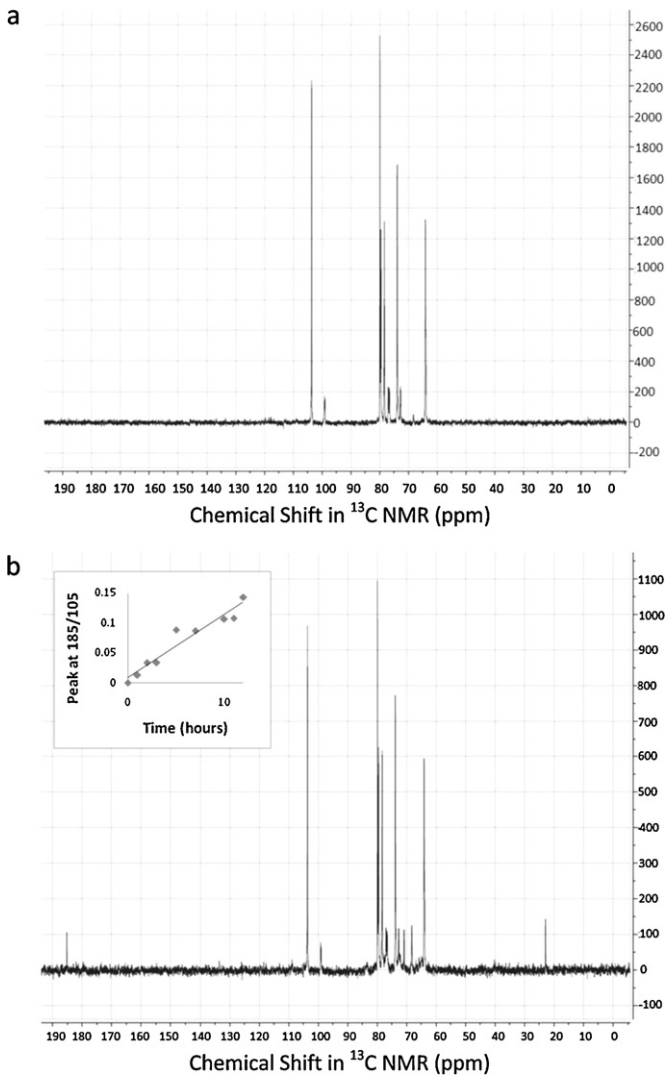


Fig. 3. ^{13}C NMR data (a) before and (b) after 11 h of cell operation.

far upfielded and is likely not attached to oxygen, which is quite interesting and requires further investigation. The NMR does confirm, however, that carbonate is not a product of this reaction under these conditions. The inset of Fig. 3(b) shows the ratio of the gluconic acid peak with the glucose peak vs. hours of cell operation, showing its continuous increase. As gluconic acid seems to be the primary product from cell reaction, it may be possible to recover the product and utilize it in some value-added downstream processes. A successful application would depend on the development of a method to separate the gluconic acid from other components in the cell, especially the dye.

Fig. 4 shows the polarization behavior in power generation and its dependence on the three different components of the cell: (a) OH^-, (b) glucose and (c) IC. All perturbations in this figure were made from a cell with 2 M NaOH, 20 mM IC and 1 M glucose. This power level can be compared to that from glucose and methyl viologen [13] and that from fructose in Fig. 5. A comparison of the maximum power and current density produced by fructose and glucose under these circumstances, as shown in Fig. 6, indicates that fructose produces higher maximum power and current densities. It should be noted that the abrupt change from the maximum power condition to short circuit is indicative that the mass transport of the reduced dyes is the rate determining step in both cases. Thus, the kinetics of the intermediate formation, charge transfer between the intermediate and dye, and between dye and current collector, are not the rate determining factors in the generation of power. This suggests that the concentration of reduced dyes (in proportion to the maximum current density) is slightly higher in the case of fructose. Such a result suggests that the turnover rate of the reduced dye formation is higher in fructose than in glucose. This is likely due to (1) a higher concentration of ene-diol intermediate (as a result of higher rate of ene-diol formation from the fructose–NaOH reaction), (2) a higher charge transfer rate between intermediate and oxidized dye, or (3) a combination of the above two factors, resulting in an increased rate of dye reduction. Thus, the slight difference between the fructose and glucose intermediate (Scheme 1) alters the reduced IC concentration in the solution. To gather evidence, comparing the ratio of power production between glucose and fructose using different dyes was further conducted.

When this experiment was performed and the ratios examined, we found that the percentage of the maximum power produced by glucose compared to that by fructose varies insignificantly among various dyes. For tryphan blue, glucose produces only 29.7% of the power density that fructose produces under the same environment. Similarly, for quanalicarin, glucose produces 22.4% of the power density that fructose produces. For IC, the result is 34.5% and for methyl viologen, 31.3%. Although these results vary, it is consistent that fructose is better than glucose in all cases. However, because these ratios are relatively close to one another, it is unlikely, for example, that IC favors the interaction between the fructose intermediate over that of glucose and that the chemical structure of quanalicarin discriminates less between the two intermediates. It is more likely that fructose has an equilibrium that leans more toward the side of the intermediate, making more intermediate available to the redox dye.

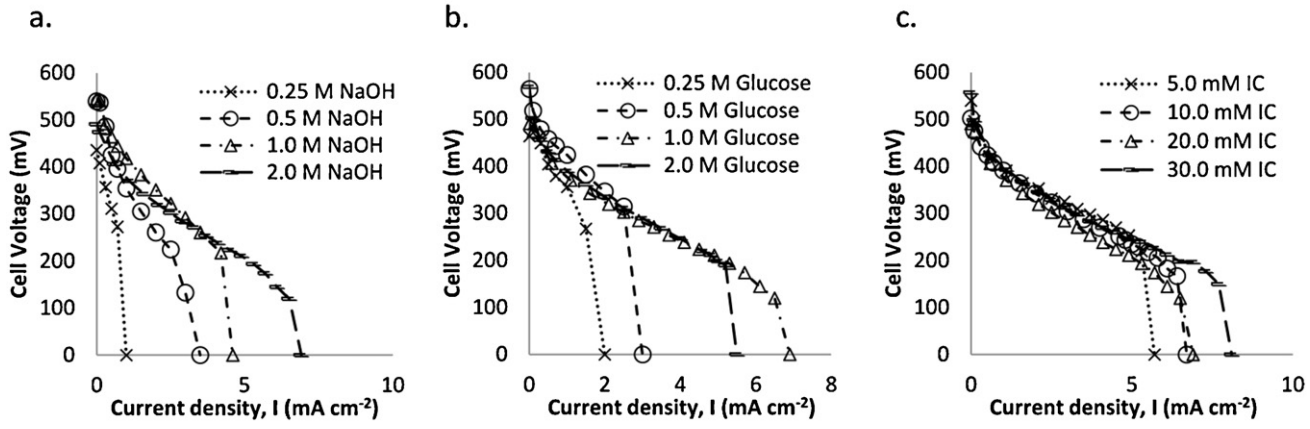


Fig. 4. Cell polarization curves with various concentrations of (a) NaOH, (b) glucose, and (c) indigo carmine.

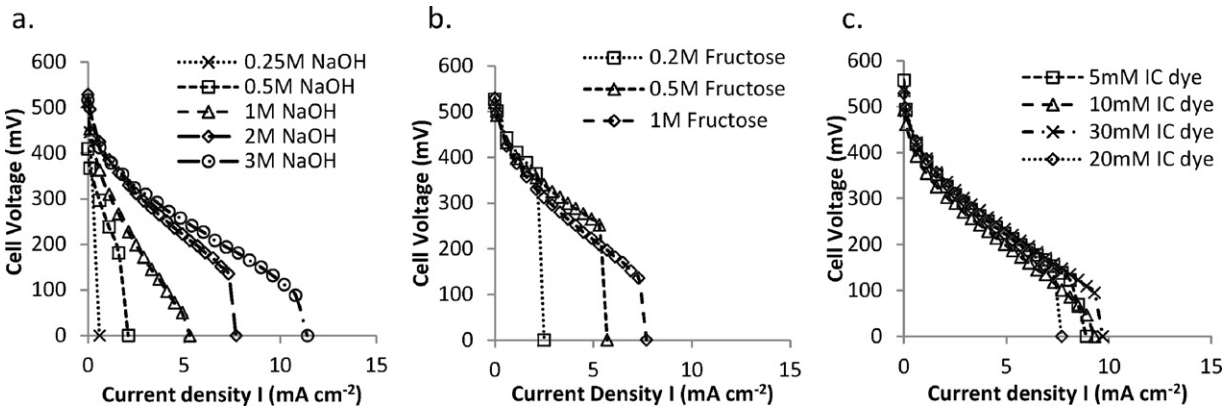
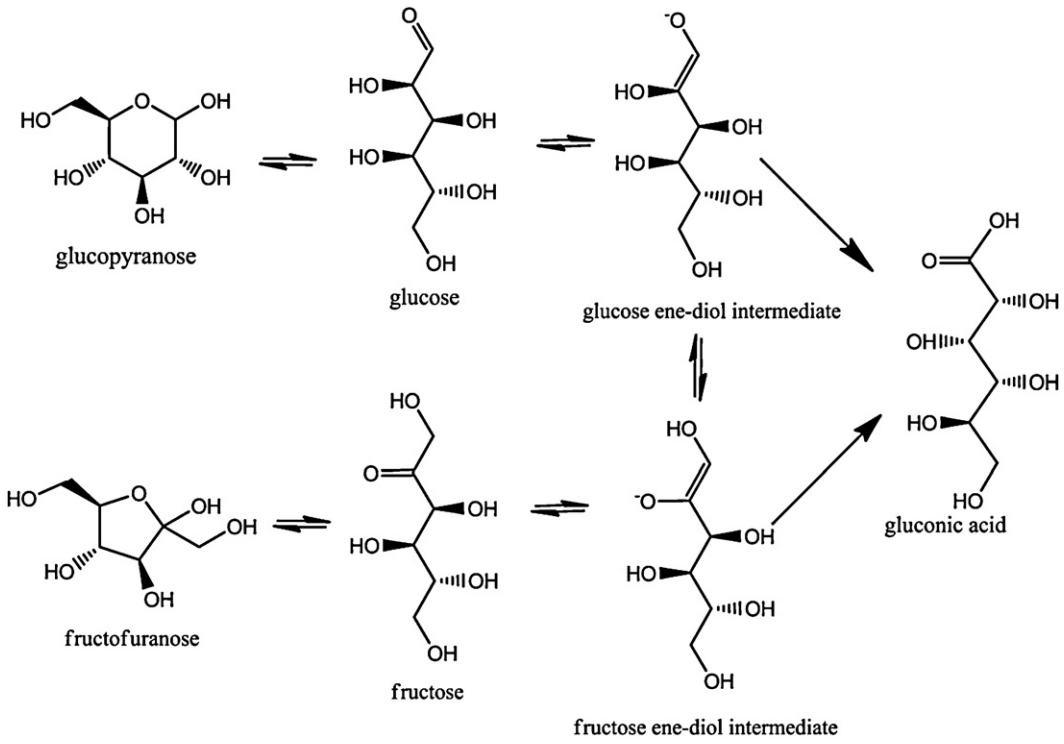


Fig. 5. Cell polarization curves with various concentrations of (a) NaOH, (b) fructose, and (c) indigo carmine.

These percentages also coincided to a degree with the lower level of the maximum power density produced by cells with different dyes. Therefore, it is comfortable to say that these percentages in reference to differences in power generation are due to the differences in rate capability by various dyes in response to increase in drawing current from a given cell configuration. To perform this experiment more effectively, it would be necessary to identify a group of dyes that are chemically different and yet produce a significant and similar amount of power, when compared to one another, with this cell configuration. The dyes chosen here are the best power producers from 45 different dyes tested. From the experiments here, it is noted that if there is a difference in the intermediate structure it cannot be concluded that different redox dyes interact more or less favorably with the different intermediates.

In previous renditions of these types of cell configurations, methyl viologen was used predominantly as the mediator dye. It is useful to note that a unique role of the strong base in this cell is to provide a favorable electrochemical potential for the oxidation of reducing sugars to reduce methyl viologen. Using a dye such as IC, whose redox potential is dependent on the concentration of base, we could study the reaction rate dependence on the concentration (thus, chemical potential) of base. Hence, we could determine the critical level of base concentration that is needed to deprotonate the reducing sugar to produce the ene-diol intermediate, providing some insight to the mechanism.

Measuring the concentration of the intermediate formed by the oxidation of reducing sugar is achieved by monitoring the visible spectral change of a solution that contains only OH^- and the sugar of interest. Fig. 7(a) shows the resulting spectra of the combinations of base with glucose, mannose and fructose, respectively. Individually, there is no significant absorbance in this region for the solution of OH^- or any of the sugars. When combined with base, all three sugars exhibit very similar absorption spectra in the visible region, indicating the formation of the ene-diol intermediates can be traced by the change of the absorbance in the spectra. Thus, the rate of the formation of these intermediates can be determined by monitoring A_{400} vs. time, as shown in Fig. 7(b). It is clear under



Scheme 1. Mechanism showing the chemical transformation of glucose and fructose to gluconic acid.

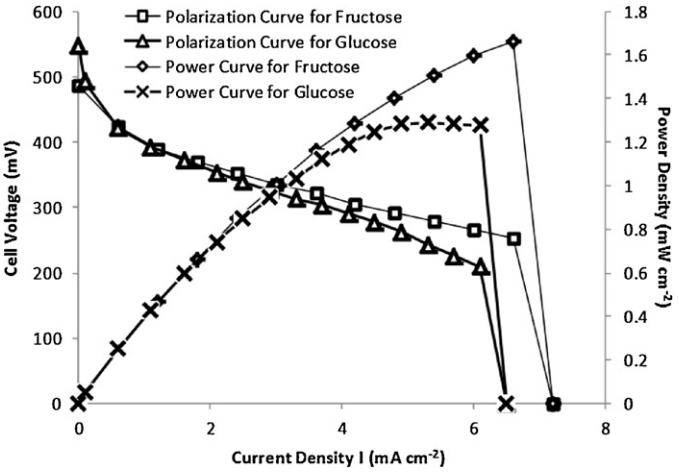


Fig. 6. Comparison of power density generated by fructose and glucose in the presence of NaOH and indigo carmine, with the maximum at about 1.7 mW cm^{-2} and 1.3 mW cm^{-2} with cell voltage of about 250 mV and 200 mV, respectively.

the same concentration of different reducing sugars, fructose has a much faster rate of intermediate formation among the three.

This is consistent with the hypothesis that as more ene-diol intermediates become available, it shall increase the rate of the re-reduction of the oxidized dyes, which should result in an enhanced current density, as evidence of higher turnover rate with fructose. On the other hand, in our experiments (as shown in Fig. 6) the overall power density in the power profile of fructose does not increase to the same degree as the rate of intermediate formation. It is likely that the amount of available dye is already maximized and that higher power density production is likely achievable by a more soluble dye. This identifies the concentration of the dye as one of the limiting factors in the amount of power that can be produced by the abiotic cells using fructose as a fuel. Fig. 7(c) also shows that as the concentration of the monosaccharide increases, less amount of base is required to reach high rates of intermediate formation. In other words, intermediate formation also depends on monosaccharide concentration. This is also consistent with increased power production at increased concentrations of monosaccharide, as we saw in Fig. 6.

The relationship between the difference in turnover rate and the mechanism of the intermediate formation is also intriguing between glucose and fructose reactions. The chemical transformation of ene-diol intermediate requires a deprotonation of one of the carbons near the carbonyl in the sugars. This deprotonation is facilitated in the case of fructose likely due to charge stabilization provided by the keto oxygen compared to that of the aldehyde carbonyl oxygen in glucose. This difference should also explain why mannose intermediate formation and power production is similar to those of glucose. The intermediates in all three monosaccharaides are obviously similar, as evidenced by the interconversion between fructose and glucose. This is further supported by the similarity in the absorption spectra for the three sugars.

It is also of interest to determine the number of electrons transferred in the sugar oxidation over long periods of time. The coulombic efficiency in the experiments is determined by the ratio of the number of electrons that result from the abiotic cells relative to the number of electrons that are theoretically available based on the concentration of glucose, assuming 2 electrons per monosaccharide molecule. These experiments, when allowed to completely discharge the cells, result in between ~97% and 130% in the coulombic efficiency calculation. The results suggest that the simple two-electron oxidation step as originally assumed might not be sufficient in explaining the cell reaction completely. More experiments to gain more details of the reducing sugar oxidation mechanism are necessary. We suspect that the additional reaction(s) that have yet to be identified may also explain the unknown compound in the NMR data. Understanding this mechanism fully would be of great value to make more electrons available from the reducing sugars.

In terms of the lifetime of such cells, the components used in the cathode and anode are primarily carbon-based and thus quite durable. Although no durability data has been shown with the cell operation, in our limited experiences, we have not observed any noticeable signs of wear and tear that could affect the cell performance from run to run. Thus, when the fuel solution is replenished, these cell components can be used repeatedly. Although there is no apparent indication that the IC is degraded under the current operating conditions, it is difficult to determine the extent of the durability and recyclability of the IC. It seems necessary to develop an effective method to separate IC from the other chemical constituents in the solution or effluent in order to recover and reuse the dye.

Scheme 1 identifies reasonable intermediates from the two different sugars and a reasonable chemical conversion to the predominant product of gluconic acid. The results of power generation obtained from the utilization of different dyes in the experiments do not suggest that the slight difference in the intermediates formed between the deprotonation of glucose and fructose is responsible for the better power production from fructose. Fructose likely produces more power than glucose because of its ability to stabilize the negatively charged oxygen of the ene-diol

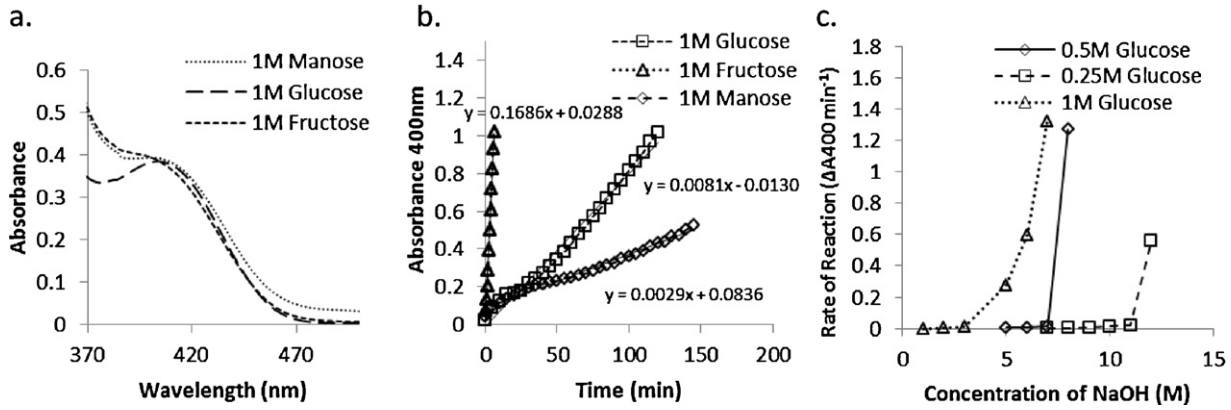


Fig. 7. (a) Absorption spectra of fructose (dashed line), glucose (solid line) and mannose (dotted line) in the presence of NaOH. (b) Increase of absorbance at 400 nm vs. time with 1 M glucose (square line), 1 M mannose (diamond line) and 1 M fructose (triangle line). (c) Rate of reaction of 0.25 M glucose (dashed line), 0.5 M glucose (solid line) and 1.0 M glucose (dotted line) with increasing concentration of NaOH.

intermediate with a secondary carbon as opposed to a primary carbon as in the case of glucose. The hypothesis that IC reactive intermediates are more stable with ene-diol motif forms on a secondary carbon also explains why power production of other aldol sugars is similar to that of glucose, as reported in Ref. [13].

4. Conclusions

The acid–base titration experiments did not indicate that there is any significant trace of CO_2 production from the abiotic cell reaction under the power generation conditions tested. The primary product revealed by the titration experiments has a pK_a consistent with that of gluconic acid. The existence of gluconic acid is further confirmed by the presence of an appropriate peak around 185 ppm in the ^{13}C NMR spectra. The NMR spectra also suggest that an additional product might exist and is yet to be identified. This unknown compound seems to have a carbon that is not attached to oxygen, and there may be more peaks masked within the carbon peaks of the glucose. The possibility of an additional reaction besides the simple two-electron reducing sugar oxidation in the charge transfer mechanism for power generation also exist, as suggested by the results of coulombic efficiency experiments, in which more than 100% in coulombic efficiency was obtained in some cases.

The utilization of fructose produces a higher power density than that of glucose. Also, the rate of intermediate formation is significantly faster in the reaction of fructose than glucose. The rate of intermediate formation depends upon the concentration of base as well as the concentration of the sugar. Although the power generation strongly depends on the concentrations of OH^- and sugar, because the dye concentration is at least an order of magnitude less, it is likely that the amount of dye as shuttle medium constrains the power generation. It also implies that significantly more power can be harnessed by increasing the concentration of dye in the solution, which needs a fundamental improvement of dye solubility in the solution. With the possibility that more than two electrons could be harvested from the reducing sugars in this abiotic cell configuration, improvement in the extent of power generation should be expected with additional optimization through the understanding of the mechanism.

Acknowledgements

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References

[1] S.C. Barton, J. Gallaway, P. Atanassov, Chem. Rev. 104 (2004) 4867–4886.
[2] S. McIntosh, R.J. Gorte, Chem. Rev. 104 (2004) 4845–4865.
[3] J. Hill, E. Nelson, D. Tilman, S. Polasky, D. Tiffany, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 11206–11210.
[4] T. Chen, S.C. Barton, G. Binyamin, Z.Q. Gao, Y.C. Zhang, H.H. Kim, A. Heller, J. Am. Chem. Soc. 123 (2001) 8630–8631.
[5] N. Mano, F. Mao, A. Heller, J. Am. Chem. Soc. 125 (2003) 6588–6594.
[6] A. Heller, Phys. Chem. Chem. Phys. 6 (2004) 209–216.
[7] E. Katz, A.N. Shipway, I. Willner, Handbook of Fuel Cells-Fundamentals, Technology, Applications, John Wiley & Sons, Chichester, PA, 2003.
[8] R.M. Allen, H.P. Bennetto, Appl. Biochem. Biotechnol. 39 (1993) 27–40.
[9] S.K. Chaudhuri, D.R. Lovley, Nat. Biotechnol. 21 (2003) 1229–1232.
[10] H. Richter, K. McKarthy, K.P. Nevin, J.P. Johnson, V.M. Rotello, D.R. Lovley, Langmuir 24 (2008) 4376–4379.
[11] S. Kerzenmacher, J. Ducree, R. Zengerle, F. von Stetten, J. Power Sources 182 (2008) 1–17.
[12] F. Matsumoto, M. Harada, N. Koura, S. Uesugi, Electrochem. Commun. 5 (2003) 42–46.
[13] D. Scott, B.Y. Liaw, Energy Environ. Sci. 2 (2009) 965–969.
[14] D.R. Wheeler, J. Nichols, D. Hansen, M. Andrus, S. Choi, G.D. Watt, J. Electrochem. Soc. 156 (2009) B1201–B1207.
[15] H.F. Cui, J.S. Ye, X. Liu, W.D. Zhang, F.S. Sheu, Nanotechnology 17 (2006) 2334–2339.
[16] S. Itoh, M. Mure, Y. Ohshiro, J. Chem. Soc.: Chem. Commun. (1987) 1580–1581.
[17] S. Shinkai, T. Kunitake, T.C. Bruice, J. Am. Chem. Soc. 96 (1974) 7140–7141.
[18] P.W. Preisler, E.S. Hill, R.G. Loeffel, P.A. Shaffer, J. Am. Chem. Soc. 81 (1959) 1991–1995.