Communication—Electrochemical Power Generation from Culled Papaya Fruits

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Low cost electric power generation using raw juice from culled papaya or fruit waste as feedstock was achieved in a sugar-air alkaline battery (SAAB) with about 37% coulombic efficiency at 0.7–0.8 mW cm–2 near peak power density. Such fruit waste, juice-based electrochemical energy could be poised as sustainable distributed energy resource for remote or underdeveloped regions that need cheap electricity without complicated infrastructure.

More than one billion people still have no access to electricity, as conventional grid-connected utility is either unavailable or cost prohibitive in many remote or underdeveloped areas globally.1 In these areas, it is extremely challenging to develop a feasible solution to provide electricity, since the energy feedstock has to be easy to obtain, store and distribute locally. Also, the system has to be easy to operate and maintain without training, advanced skill set, and infrastructure.

Abiotic reducing sugar-air alkaline battery (SAAB) or fuel cell (SAFC) systems (Figure 1) recently have been shown capable of harnessing electric power from partial oxidation of various reducing sugars using strong base solutions and mediator dyes.2–6 The reaction mechanism of SAAB is discussed in detail by Scott et al.7 The SAAB uses inexpensive electrode materials in concentrated potassium or sodium hydroxide solution, in one compartment2,4,5 without using expensive separators (e.g. Nafion) or (bio-)catalysts. Methyl viologen (MV) and indigo carmine (IC) are among the best mediators for charge transfer.

For practical use, cheap feedstock is essential. A significant quantity of unmarketable culled papaya and processing waste are available in Hawaii and many other regions around the globe, especially in developing economies. Instead of subjecting the fruit waste to microbial fermentation to make biogas, ethanol, or lipids as biofuels, they can serve as cheap feedstock for SAAB to generate electricity. Microbial fermentation of papaya fruit wastes for biofuels or bioenergy requires substantial infrastructure and water- and energy-demanding processing. Furthermore, fermentation is sensitive to environmental factors (e.g. temperature and humidity) and impurities (e.g. inhibitors in fruit wastes could impair ethanol or lipid production). The SAAB, in contrast, is very forgiving in the quality of sugar feedstock, and hence the cost (i.e. $ kg–1 for feedstock and $ kWh–1 for electricity) and complexity of the energy harvesting process could be drastically reduced.

Papaya has high content of glucose and fructose,7 and polysaccharides that could be hydrolyzed to form reducing sugars, making it attractive for fueling SAAB operation.

Experimental

Solo papayas (Kahuku farms, Kahuku, Hawaii) were used in all experiments and were fully ripe with bright yellow color when used. Papaya fruits were processed in three different ways to generate: (i) puree without removal of either seeds or peels (“seeds”), (ii) puree with seeds removed (“no seeds”), and (iii) supernatant from centrifugation of “no seeds” samples to remove the fruit pulps (“clarified”). A fourth sample is a sugar solution containing 45 g L–1 of fructose and glucose, respectively (“sugar”), totaling 0.5 M in sugar content, to match sugar composition of papaya samples determined using HPLC (data not shown).

To characterize sugar composition using HPLC, clarified papaya juice samples were centrifuged, the resulting supernatant filtered, and loaded into a Waters 2695 HPLC connected to a Waters 410 differential refractometer (Waters, Milford, MA). Sugars were separated with a Rezex RPM Monosaccharide column (Phenomenex, Torrance, CA) using deionized and degassed water as an eluent. Reducing sugar concentrations in the samples were measured using the dinitrosalicilic acid method (DNS method).8

A SAAB cell modified from the original design by Scott and Liaw9 was used in the experiments (shown schematically in Figure 1). The anode was carbon felt and the cathode an air-breathing electrode plate with manganese oxide catalyst on carbon support and Teflon backing (Electric Fuel, Israel). Pt wire was used to make electrical contact. Papaya feedstock was mixed and made into 3 M KOH and 20 mM MV or IC solution. Cell performance, including open circuit voltage (OCV), limiting current density (iL), and peak power density (PPD), were determined using a Bio-Logic VMP3 workstation in chronopotentiometric mode. After priming at open circuit for 30 min, the current in 0.250 mA increments (0.197 mA cm–2) was imposed on the cell at 30 min intervals to record the terminal voltage for the polarization curve. The limiting current was recorded at zero volts. The cathode cross section exposed to the solution was used in the calculation of iL and PPD. A stack was tested using the same protocol and a master channel with two slaves configured to measure four cells of “no seeds” sample in series. Coulombic efficiency, Ah L–1, and Wh L–1 were determined using constant current discharge near peak power.

Figure 1. Schematic of the sugar-air alkaline battery/fuel cell for power generation.

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Figure 2. Polarization and power density curves for papaya treatments and sugar water as reference, using 20 mM MV as mediator, as well as “no seeds” treatment without mediator addition. Solid lines correspond to cell voltage, and dashed lines represent the power density.

Figure 3. Polarization and power density curves for a stack of four cells in series with “no seeds” samples. Cells were loaded with 2 ml of “no seeds” juice, 20 mM MV and 3 M KOH. White and black symbols represent power and voltage, respectively.

Figure 4. Polarization and power density curves for papaya treatments and sugar water as reference, using 20 mM of IC as mediator. Solid lines correspond to cell voltage, and dashed lines represent the power density.

Results and Discussion

Figure 2 exhibits the polarization curves and power profiles of the four groups of sample using MV as mediator, plus a “no seeds” sample without mediator addition. Figure 3 is the polarization curve of the four-cell stack, demonstrating a reliable operation to meet power demands. Figure 4 shows the polarization curves and power profiles of cells with the four groups of samples using IC as mediator. Table I summarizes the performance metrics for all samples using MV as mediator.

Table I. Performance metrics of the SAAB tested with four different groups of samples: seeds, no seeds, clarified, and sugar solution, each with 20 mM methyl viologen and 3 M KOH.

|                   | Seeds          | No Seeds       | Clarified      | Sugar          |
|-------------------|----------------|----------------|----------------|----------------|
| Ah L⁻¹             | 6.40 ± 1.08    | 8.53 ± 2.68    | 12.09 ± 2.63   | 10.70 ± 1.47   |
| Wh L⁻¹             | 2.21 ± 0.60    | 2.79 ± 0.56    | 4.57 ± 1.06    | 4.61 ± 0.80    |
| Coulombic efficiency (%) | 28 ± 4 | 28 ± 2 | 37 ± 4 | 38 ± 2 |
| Sugar content (g L⁻¹) | 71 ± 2 | 82 ± 4 | 91 ± 3 | 90 |

*Under peak power condition.

Previous studies²,⁴,⁵ showed that the type and concentration of reducing sugar, the alkaline concentration, and the type and concentration of mediator all affect the cell performance. Sugar content increases slightly with the extent of juice pretreatment, as shown in Table I. The three different juice pretreatments however give similar PPD at 0.75–0.81 mW cm⁻². When no mediator was used with the “no seeds” samples, PPD at 0.53 mW cm⁻² could still be obtained, indicating the presence of endogenous electron mediators in papaya juice that could assist charge transfer, a phenomenon that was not found in purified sugar solutions. Further studies are underway to identify the species and mechanism associated with it. The higher sugar content in the clarified juice and sugar solution vs. non-clarified juice samples does lead to higher energy density (Wh L⁻¹) and useful capacity (Ah L⁻¹), as exhibited in Table I, when discharged near peak power. Also, a difference in coulombic efficiencies between the clarified juice (including sugar reference) and non-clarified juice treatments is noted in Table I.

The coulombic efficiency could be affected by a number of factors, such as temperature, discharge rate, cell internal resistance, and the extent of undesirable side reactions, as reported by Orton and Scott between 15°C–49°C using different mediators.⁹ We observed during SAAB disassembly that pulps tend to settle out of solution, partly clogging the pore channels and blocking the surface of the carbon electrode. The presence of solid suspension in pulp could inhibit mass transport of the mediator (due to variations in tortuosity and pore clogging that reduce the flux to the anode) or lead to surface area reduction for charge transfer. Based on results from the polarization curves (Figures 2 and 4), the presence of fruit pulp in the sample does not appear to affect dye mass transfer substantially. Lower coulombic efficiency is likely attributed to reduction of effective electrode surface area. However, the cell assembly could withstand repetitive use in testing without fouling in the cell operation and electrode performance, since pulp settlement can be removed easily, as electrodes were rinsed lightly in water between runs.

The energy conversion efficiency of the system could be improved by agitation, which increases both PPD and coulombic efficiency.² This efficiency is sensitive to current density, solution composition (e.g. adding a co-solvent to the solution⁵ to reduce internal resistance), and other operating conditions (e.g. temperature⁹).
The stacking of cells in series exhibits no compromise in performance, indicating that scaling up operation is possible (Figure 3). When IC, an FDA approved food dye (FD&C #2), was used as a mediator, similar performance can be achieved, as shown in Figure 4, making the cell more environmentally friendly to operate.

Conclusions

The power generation (0.75–0.81 mW cm⁻²) using culled papaya or its waste in sugar-air alkaline battery is feasible and the coulombic efficiency (30–40%) obtained using clarified juices is as high as purified sugar solutions near peak power. Pulp might cause marginal variations in cell performance, but does not foul the electrodes or cell durability. The system is highly scalable. Safer mediators, such as indigo carmine, make the system environmentally friendly. Finally, we would like to emphasize the significance of this work as an innovative concept of a sustainable energy conversion pathway that builds on the simplicity in cell configuration and operation to achieve cost reduction and high efficiency, and may provide a solution for solving the needs of over one billion people who still have no access to electricity.

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