WATER RESEARCH 42 (2008) 1501–1510

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Evaluation of energy-conversion efficiencies in microbial fuel cells (MFCs) utilizing fermentable and non-fermentable substrates

Hyung-Sool Lee, Prathap Parameswaran, Andrew Kato-Marcus, César I. Torres, Bruce E. Rittmann*

Center for Environmental Biotechnology, The Biodesign Institute at Arizona State University, 1001 S. McAllister Avenue, Tempe, AZ 85287-5701, USA

ARTICLE INFO

Article history:
Received 7 August 2007
Received in revised form
18 October 2007
Accepted 23 October 2007
Available online 1 November 2007

Keywords:
Electron-equivalent balance
Energy-conversion efficiency
Potential efficiency
ARB density
Concentration gradient

ABSTRACT

We established the first complete electron-equivalent balances in microbial fuel cells (MFCs) fed with non-fermentable (acetate) and fermentable (glucose) electron donors by experimentally quantifying current, biomass, residual organic compounds, H_2, and CH_4 gas. The comparison of the two donors allowed us to objectively evaluate the diversion of electron flow to non-electricity sinks for fermentable donors, leading to different behaviors in energy-conversion efficiency (ECE) and potential efficiency (PE). Electrical current was the most significant electron sink in both MFCs, being 71% and 49%, respectively, of the initial COD applied. Biomass and residual organic compounds, the second and third greatest sinks, respectively, were greater in the glucose-fed MFC than in the acetate-fed MFC. We detected methane gas only in the glucose-fed MFC, and this means that anode-respiring bacteria (ARB) could out-compete acetoclastic methanogens. The ECE was 42% with acetate, but was only 3% with glucose. The very low ECE for glucose was mostly due to a large increase of the anode potential, giving a PE of only 6%. Although the glucose-fed MFC had the higher biomass density on its anode, it had a very low current density, which supports the fact that the density of ARB was very low. This led to slow kinetics for electron transfer to the anode and accentuated loss due to the substrate-concentration gradient in the anode-biofilm. The large drop of PE with low current, probably caused by a low ARB density and electron (e^-) donor concentration, resulted in a poor maximum power density (9.8 mW/m^2) with glucose. In contrast, PE reached 59% along with high current for acetate and the maximum power density was 360 mW/m^2.

1. Introduction

Approximately 86% of world energy production comes from fossil fuels today (Energy Information Administration, 2005), but fossil fuels, especially petroleum, are being exhausted, leading to an energy crisis in the near future (Rifkin, 2002). Furthermore, the combustion of fossil fuels adds CO_2 to the atmosphere and causes global climate change (IPCC, 2007). To mitigate the adverse effects of an energy crisis and global climate change, society needs to develop carbon-neutral, sustainable energy sources as alternatives to fossil fuels.

Biomass is proposed as one of the future energy sources, since it is carbon-neutral. However, biomass energy is used today mostly through combustion, which emits local air

*Corresponding author. Tel.: +1 480 727 0849; fax: +1 480 727 0889.
E-mail addresses: hyungsool@asu.edu (H.-S. Lee), Prathap.Parameswaran@asu.edu (P. Parameswaran), Andrew.Marcus@asu.edu (A. Kato-Marcus), Cit@asu.edu (C.-I. Torres), Rittmann@asu.edu (B.E. Rittmann).
0043-1354/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2007.10.036

pollutants that threaten human and ecological health (EIA, 2006). A means to capture the energy values in biomass without combustion would provide sustainable energy for global society without causing local pollutant problems.

The energy value of biomass comes about because its carbon molecules contain high-energy electrons. Microorganisms can channel the electrons and their energy to forms that human society can use readily: methanogenesis to CH_4, biohydrogen to H_2, and microbial fuel cells (MFCs) to electricity. Among these alternatives, MFCs are attractive because they produce society's most widely useful energy form—electricity—directly without combustion. Due to their potential advantages, MFCs have gained much attention in recent years (e.g., Logan, 2004; Rabaey and Verstraete, 2005; Rittmann, 2006; Buckley and Wall, 2006; Lovley, 2006).

Power, the rate of energy generation, is an essential gauge of the electricity-supplying capacity for an MFC. Despite important scientific advances, the power density of MFCs (expressed as W/m^3 or W/m^2) is still insufficient for practical energy supply. Rabaey et al. (2003) reported the highest volumetric power density, $275\,W/m^3$, using glucose, but others reported power densities one or two orders of magnitude less using glucose (Liu and Logan, 2004; Min and Logan, 2004; Chaudhuri and Lovley, 2003; Bond and Lovley, 2003). The maximum power density was increased up to $1\,kW/m^3$ using acetate at the bench scale (Fan et al., 2007). For comparison, the power density from MFCs is smaller than what is generated from methanogenesis: 1–5 kW/m^3 in full-scale anaerobic digestion (Van Lier, 2007). For MFCs to become a practical energy source, their power density must be improved by 10- to 100-fold.

Power density is not the only evaluation criterion for MFCs. Another criterion is the energy-conversion efficiency (ECE), or the fraction of energy in a fuel that is captured in the electricity output. Heat engines typically have an ECE of ~33% (Sun et al., 2004), while hydrogen fuel cells have about 55% (Larminie and Dicks, 2003). Rabaey et al. (2003) reported a 65% ECE in a batch MFC, but an ECE as low as 0.3% was reported for a continuous MFC (Min and Logan, 2004). One reason for a low ECE is that large amounts of residual organics are discharged from the MFC. When the MFC is used as part of waste treatment, this form of inefficiency means that the MFC has failed in its treatment role, as well as in its role of an energy producer.

The ECE value in an MFC is the product of its coulombic efficiency (CE) and potential efficiency (PE) for the electrons captured as electrical current. Specifically, CE is the fraction of electrons transferred to the MFC anode from e^- donor applied, while PE is the fraction of the potential difference captured as useful electrical energy in comparison to the potential difference between the e^- donor and acceptor. Thus, ECE can be expressed mathematically by

$$\mathrm{ECE} = \frac{P\Delta t}{e^-_{\mathrm{donor}}(-\Delta G'^{o}_{\mathrm{rxn}})} = \frac{I\Delta t V_{\mathrm{meas}}}{e^-_{\mathrm{donor}}(-\Delta G'^{o}_{\mathrm{rxn}})} = \frac{e^-_{\mathrm{trans}}}{e^-_{\mathrm{donor}}}\frac{V_{\mathrm{meas}}}{V_{\mathrm{reac}}} = \mathrm{CE}\times\mathrm{PE}, \quad (1)$$

where P is the power (J/s), Δt the reaction time (s), e^-_{donor} the electron equivalents of initial substrate, $\Delta G'^{o}_{\mathrm{rxn}}$ the change in standard Gibb's free energy at pH 7 between the e^- donor and acceptor (J/e^- eq), I the current (C/s), e^-_{trans} the electron equivalents transferred to the anode during the reaction time, V_{meas} the measured voltage output (J/C), V_{reac} the $-\Delta G'^{o}/F$ (J/C), and F the Faraday constant (96,485 C/e^- eq).

ECE values reach a maximum only when CE and PE are high together. However, PE is negatively correlated with current density, which is a factor needed to optimize the power density (Liu and Logan, 2004; Rabaey et al., 2005a; Jong et al., 2006; Logan et al., 2007). For this reason, the best way to have high ECE and high power density is to maximize CE at the optimum power density.

CE seems to depend on substrate type. Acetate appears to be the best substrate, with CEs ranging from 65% to 84% (Min and Logan, 2004; Liu et al., 2005; Rabaey et al., 2005a; Torres et al., 2007). The CE dropped to 14–20% for glucose (Min and Logan, 2004; Liu and Logan, 2004) and to 8% for wastewater (Min et al., 2005). The sharp decline in CE for the more complex organics suggests that competing electron sinks are important. Biomass, soluble organic products, H_2, and CH_4 are possible electron sinks in MFCs if exogenous e^- acceptors, particularly oxygen, do not enter the anode compartment. Electron equivalents for the gases can be considerable for MFCs fed with fermentable substrates, as compared to non-fermentable substrates, since H_2 is normally produced in fermentation. And, H_2 is a good electron donor for methanogens to produce CH_4, a factor that is supported by CH_4 detection in MFCs fed with glucose, but not in acetate-fed MFCs (Freguia et al., 2007; Torres et al., 2007). Furthermore, fermentation is performed by diverse microorganisms that have higher growth yields than do anode-respiring bacteria (ARB) (Esteve-Núñez et al., 2005; IWA, 2002), and their high yield can make biomass a significant electron sink that reduces CE. Despite the significance of tracking the fate of all electron equivalents in MFCs, no experimental studies have quantified electron sinks and completed an electron-equivalent balance.

In conventional fuel cells, the PE is normally decreased by three kinds of energy losses, or over-potentials: ohmic, concentration, and activation (Larminie and Dicks, 2003; Logan et al., 2006). Ohmic losses occur due to the current resistance in the electrodes and interconnection circuit, as well as resistance to ion flow in the electrolyte and through the cation exchange membrane (CEM). Concentration losses occur when the oxidation of fuel at the anode or the reduction of oxidant at the cathode is much faster than the transfer rates of fuel or oxidant to the electrode. Generally, concentration losses become important with high current density, for which the concentration of fuel or oxidant must be much lower at the electrode to drive the high rate of mass transfer. Rabaey et al. (2005b) argued that MFCs do not generate high enough current density to cause significant concentration losses. Activation losses occur during electron transport from the e^- donor to the anode or from the cathode to the oxidant to gain a certain current in a fuel cell. For conventional fuel cells, activation loss is a means to include the local concentration at the electrode without needing to determine the local concentration.

For an MFC, energy losses associated with the anode (i.e., the anode over-potential) cannot be described only with the conventional energy losses. Formation of the anode-biofilm leads to a different environment from a conventional fuel cell.