

Production of Electricity during Wastewater Treatment Using a Single Chamber Microbial Fuel Cell

HONG LIU,[†]
RAMANATHAN RAMNARAYANAN,[‡] AND
BRUCE E. LOGAN^{*,†,§}

Department of Civil and Environmental Engineering,
Department of Chemistry, and The Penn State Hydrogen
Energy (H₂E) Center, The Pennsylvania State University,
University Park, Pennsylvania

Microbial fuel cells (MFCs) have been used to produce electricity from different compounds, including acetate, lactate, and glucose. We demonstrate here that it is also possible to produce electricity in a MFC from domestic wastewater, while at the same time accomplishing biological wastewater treatment (removal of chemical oxygen demand; COD). Tests were conducted using a single chamber microbial fuel cell (SCMFC) containing eight graphite electrodes (anodes) and a single air cathode. The system was operated under continuous flow conditions with primary clarifier effluent obtained from a local wastewater treatment plant. The prototype SCMFC reactor generated electrical power (maximum of 26 mW m⁻²) while removing up to 80% of the COD of the wastewater. Power output was proportional to the hydraulic retention time over a range of 3–33 h and to the influent wastewater strength over a range of 50–220 mg/L of COD. Current generation was controlled primarily by the efficiency of the cathode. Optimal cathode performance was obtained by allowing passive air flow rather than forced air flow (4.5–5.5 L/min). The Coulombic efficiency of the system, based on COD removal and current generation, was <12% indicating a substantial fraction of the organic matter was lost without current generation. Bioreactors based on power generation in MFCs may represent a completely new approach to wastewater treatment. If power generation in these systems can be increased, MFC technology may provide a new method to offset wastewater treatment plant operating costs, making advanced wastewater treatment more affordable for both developing and industrialized nations.

Introduction

Over 126 billion liters of domestic wastewater is treated each day in the U.S. at an annual cost of over \$25 billion (1). Most of this wastewater is sent to centralized facilities that consume large amounts of energy for treatment due to aeration. These high energy costs for sanitation to levels required in the U.S. cannot be borne by a global population of six billion people, particularly in developing countries. Anaerobic treatment technologies provide potential for reducing treatment costs,

but these technologies are generally only suitable for high-strength wastewater streams typically produced by industry. In addition, conventional anaerobic treatment produces methane gas, which if released, can contribute to global warming. One method has been advocated to reduce wastewater treatment costs, finding ways to produce useful products from wastewater treatment (2). However, effective methods for generating products other than methane from wastewater have not yet been shown to be feasible.

It has been known for several years that bacteria can be used to generate electricity that can be harvested in microbial fuel cells (MFCs) (3). In a MFC, bacteria that oxidize a substrate are kept physically separated from the electron acceptor by a proton exchange membrane. Electrons pass from the bacteria to the electrode (anode) in the same chamber and then via a circuit to the cathode where they combine with protons and oxygen to form water. The difference in the potential coupled to electron flow produces electricity in this fuel cell. Electrons generated by bacteria through the anaerobic oxidation of organic matter (by nonfermentative reactions) are passed to respiratory enzymes normally bound to the inner cell membrane. Artificial electron carriers (mediators), such as neutral red or anthraquinone-2,6-disulfonate (AQDS), or high concentrations of humic acids can be used to carry electrons from inside the cell to an external electrode (3–6). However, the need for high concentrations of electron carriers, many of which are toxic chemicals, is thought to make electricity generation on a large scale in a mediator-type fuel cell impractical. Some bacteria, such as *Shewanella putrefaciens*, however, can produce their own mediators (soluble quinones) (7) that can eliminate the need to add mediators.

It was only recently discovered that the respiratory enzymes of certain iron-reducing bacteria span their outer membrane allowing direct transfer of electrons to external metals such as Fe (III) or Mn (IV) (8–10). The attachment of these iron-reducing bacteria to carbon electrodes results in electron transfer to the anode, with oxygen reduction at the cathode (11). The measured equilibrium potentials (–0.17 V) are close to those of purified preparations of *c*-type cytochromes (–0.19 V) used in the respiratory chains of these bacteria, suggesting these enzymes are responsible for electron transfer to the electrode (11). Power generated in various types of MFCs systems vary widely as a function of the inoculum, substrate, and reactor, ranging from <1 mW/m² (12) with lactate and pure cultures of *S. putrefaciens* to 3600 mW/m² with glucose and an unidentified mixed culture (13). Most results with carbon electrodes generally report power generation rates on the order of 10–100 mW/m² (5, 11, 14–16).

It has not previously been examined whether electricity can be generated using domestic wastewater or if MFCs could be used for domestic wastewater treatment. In addition, current designs for mediator-less MFCs have not been developed specifically for continuous wastewater treatment. Two types of MFCs have so far been used: small batch-fed laboratory systems primarily using defined substrates and MFCs developed to harvest energy from marine sediments. Laboratory systems typically use separate compartments for the anode and cathode connected by a proton exchange membrane (PEM) (11, 14). This two-compartment design would be difficult to apply to larger systems for continuously treating wastewater. Marine sediment systems are based on the placement of a carbon pad into an anaerobic sediment (anode) and a second pad placed in overlaying oxygenated waters (cathode) (5, 17). The latter systems cannot be adapted

* Corresponding author phone: (814)863-7908; fax: (814)863-7304; e-mail: blogan@psu.edu.

[†] Department of Civil and Environmental Engineering.

[‡] Department of Chemistry.

[§]The Penn State Hydrogen Energy (H₂E) Center.

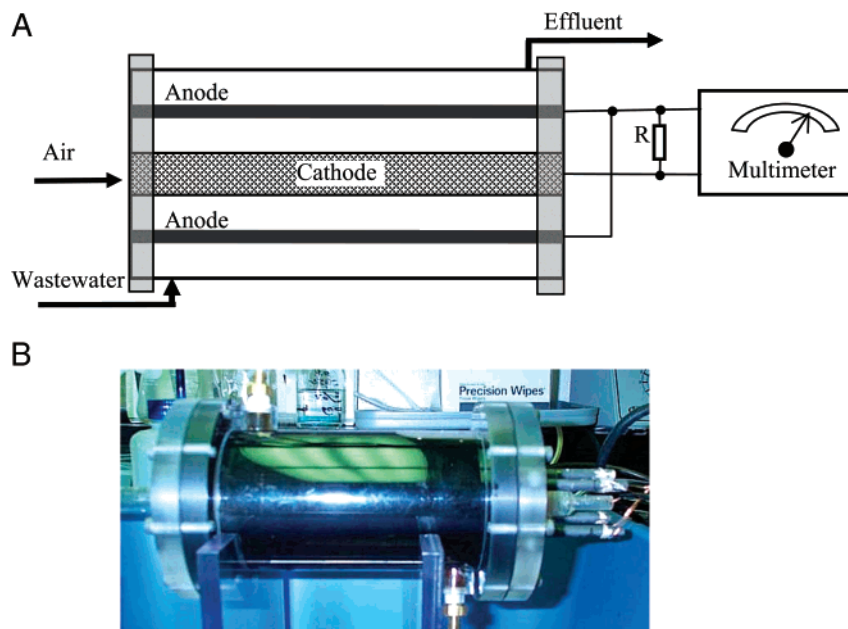


FIGURE 1. (A) Schematic and (B) laboratory-scale prototype of the SCMFC used to generate electricity from wastewater.

for continuous treatment of a wastewater due to the need for large volumes of oxygenated water and the limited solubility of dissolved oxygen in water. Thus, changes in reactor design are needed to produce MFCs suitable for treating continuous streams of dissolved organic matter.

To continuously generate electricity from organic matter in water, a MFC reactor must have both a large surface area for biofilm formation and a high void volume. Lessons learned from the design of fixed-film bioreactors used for wastewater treatment can be applied to MFCs. Wastewater treatment reactors are designed to be highly porous to avoid clogging the reactor with high concentrations of particles in the wastewater. This requirement for high porosity is at odds with the need for a large surface area for biofilm formation. Thus, fixed-film wastewater reactors have been designed to produce thin fluid films and convective flow rates sufficiently high to shear off excess biofilm growth from surfaces. These reactors cannot be used without modification for energy production because MFCs have an additional requirement that the biomass be kept separated from any dissolved oxygen. These design challenges are similar to requirements for membrane bioreactors used to treat water and wastewater. In these reactors, a series of fibrous nanopore-sized membranes are inserted into a single, sheared compartment providing a high porosity tank containing the membrane (18). The high shear generated in the reactor by bubbles is used to help shear biofilms from the fibers.

The methods used to achieve a high porosity in membrane reactors suggested a method to improve the design of a MFC by providing a chamber that contained both the anode and the cathode in a single compartment MFC (SCMFC). A prototype reactor was built and tested using wastewater obtained from a local wastewater treatment plant. We report here our preliminary findings using this reactor that demonstrate for the first time electricity generation accompanied by wastewater treatment demonstrated by the removal of organic matter in the form of chemical oxygen demand (COD) or biochemical oxygen demand (BOD).

Materials and Methods

The SCMFC consisted of a single cylindrical plexiglass chamber (15 cm long by 6.5 cm diameter; empty bed volume of 388 mL) containing eight graphite rods (anode) each 6.15 mm in diameter and 150 mm long (Alfa Aesar, Ward Hill,

MA) placed in a concentric arrangement about a single cathode (Figure 1). The graphite rods were abraded by sand paper to enhance bacterial attachment. The air-porous cathode consisted of a carbon/platinum catalyst/proton exchange membrane (PEM) layer fused to a plastic support tube. The PEM (Nafion 117, Dupont, Wilmington, DE) was sequentially boiled in H₂O₂ (30%), deionized water, 0.5 M H₂SO₄, and then deionized water (each time for 1 h). The PEM was then hot pressed directly onto carbon cloth loaded with 0.5 mg cm⁻² of Pt (E-Tek, Miami, FL) by heating it to 140 °C at 1780 kPa for 3 min. The cathode/PEM was placed onto a 25 mm diameter plastic (Plexiglas) tube containing 2 mm diameter pores at 2 mm intervals (cathode tube). Air flow through the tube was initially 4.5–5.5 mL/min but was changed to passive oxygen transfer (no forced air flow) except as noted. Copper wire was used to connect the circuit containing a 465 Ω load unless stated otherwise.

Local domestic wastewater (primary clarifier effluent) was obtained from the primary clarifier of the Pennsylvania State University Wastewater Treatment plant. Wastewater was pumped into the reactor and used as the fuel without any modifications except for dilution of the wastewater with deionized water in some experiments. Wastewater fed to the reactor had a pH ranging from 7.3 to 7.6 and a COD of 210 or 220 mg/L. The hydraulic retention time in the reactor ranged from 3 to 33 h as noted. All measurements were taken after the reactor had been operated for at least six hydraulic retention times, when power output was consistent. Measurements reported here are averages of triplicate measurements taken over three consecutive retention times. Two different controls were used to account for COD losses. The first control consisted of a second tank of similar volume (400 mL) to account for COD or BOD losses unrelated to fuel cell operation (volume control). The second control consisted of a separate set of experiments using the SCMFC with an open circuit (disconnected electrodes; electrode control). All experiments were conducted in a temperature-controlled room set at 30 °C.

In the first set of experiments, the SCMFC was inoculated with a pure culture (*Geobacter metallireducens*, 10 mL at 0.5 g-DW/L), filled with wastewater, and operated in batch mode for one week. However, other experiments in our laboratory and by others (19) demonstrated that this inoculation step was not needed to produce electricity in a MFC. Therefore,

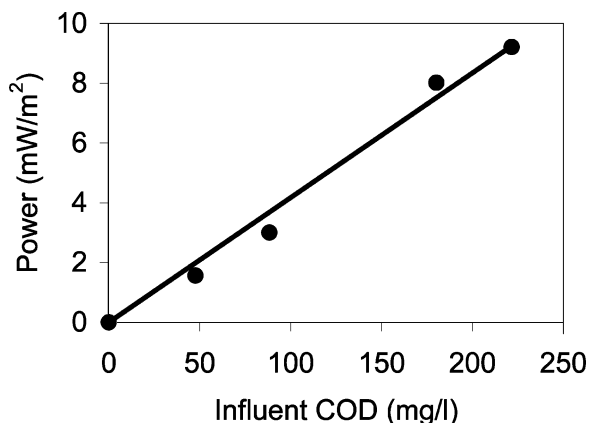


FIGURE 2. Power generated in a SFMFC as a function of influent wastewater concentration (465 Ω , HRT = 12 h, and air flow rate of 5.5 L/min; reactor initially inoculated with *G. metallireducens*).

except as stated otherwise, the SCMFC was inoculated using only the bacteria present in the wastewater.

Oxygen transfer through the membrane was estimated based on measurements of oxygen flux through Nafion membranes in hydrogen fuel cells (20). The rate (W) of oxygen transfer through a membrane is a product of the cross section A and flux (J), or

$$W = JA = -DA \frac{dC}{dx} \cong -DA \frac{\Delta C}{\Delta x} \quad (1)$$

For a cross-sectional area of 102 cm², and assuming saturation of oxygen in the membrane ($3.7\text{--}6.2 \times 10^{-7}$ mol/cm³), no oxygen in the anode section, a membrane thickness of 190 μ m, and diffusion constants of oxygen in the membrane that range from 1 to 6×10^{-6} cm²/s (20), oxygen transport into the anode chamber would range from 0.23 to 2.3 mg of O₂/h.

Analyses. Voltage was continuously measured by a multimeter with a data acquisition system (2700, Keithly, Cleveland, OH) and converted to power according to $P = iV$, where P = power, i = current, and V = voltage. Power was normalized by the total surface area of the anodes. COD and BOD were measured according to standard methods (21). Total electron flow was calculated by summing the product of the time interval and the current passed through the circuit. Coulombic efficiency was calculated as the total coulombs measured divided by the moles of COD removed assuming 4 mol of electrons/mol of COD.

Results and Discussion

Electricity in the SCMFC was generated using domestic wastewater in proportion to wastewater strength (Figure 2). The voltage across the circuit containing a 465 Ω resistor increased to 0.32 V for wastewater containing up to 220 mg/L of COD, producing up to 9 mW/m² of power based on anode surface area (HRT = 12 h; air flow rate = 5.5 L/min). Organic matter removal in terms of BOD was nearly constant at $78 \pm 2\%$, while the reduction in COD ranged from 50 to 70% (Figure 3). Changes in the amount of BOD removed relative to COD removed reflect differences in the biodegradability of the wastewater samples fed to the reactor, large statistical variations in BOD test results ($\pm 20\%$ even at a single laboratory), and some losses of BOD that may have occurred in the volume-control tank (no electrodes) (5–20% variation in BOD). Not all of the organic matter in a wastewater can be biologically degraded, so that COD removals are typically lower than those for BOD removal (21).

Forced air flow through the cathode tube was found to decrease power generation (Figure 4). Compared to passive air flow, forcing air through the cathode tube at 4.5 L/min

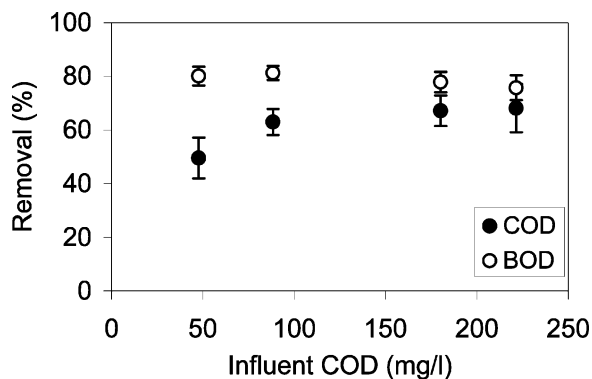


FIGURE 3. Removal of organic matter in terms of COD (●) and BOD (○) by the SCMFC as a function of wastewater strength (465 Ω , HRT = 12 h, and air flow rate of 5.5 L/min; reactor initially inoculated with *G. metallireducens*). (Error bars \pm SD based on triplicate measurements of the reactor effluent.)

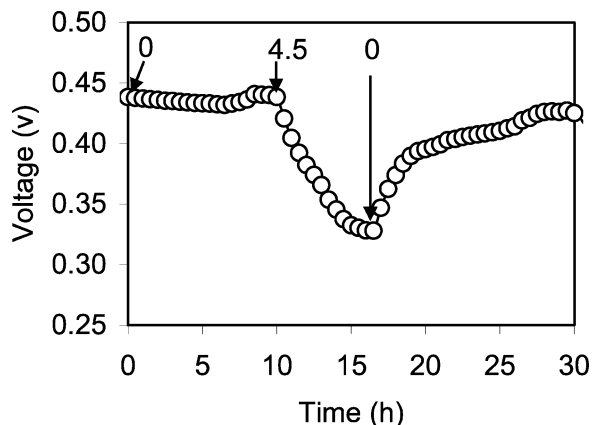


FIGURE 4. Effect of oxygen flow on electricity generation (HRT of 3 h). Values indicate air flow rate (L/min) (COD = 210 mg/L, 465 Ω).

decreased the voltage in the reactor by 25% over a 7.5 h period. Therefore, in subsequent experiments only passive air transfer was used at the cathode.

Power output was a function of circuit load (16–5000 Ω) in the system, consistent with trends observed by others in other MFC experiments (11, 23). At a hydraulic detention time of 6 h, power reached a maximum of 26 mW/m², with a current density of 125 mA/m² (69 Ω resistor) in the absence of forced air flow through the cathode tube (Figure 5). In contrast, a maximum of only 12.2 mW/m² was achieved in the system with air flow at 5.5 L/min at a longer detention time (HRT = 12 h).

COD removal and power were a function of hydraulic detention times of the wastewater in the reactor. COD removal increased from 40% at a HRT = 3 h to a maximum of 80% at a HRT of 33 h (passive air cathode; 465 Ω) (Figure 6). A large percent of the COD removal was not associated with power generation. When the circuit was disconnected, COD removal ranged from 20 to 50% over the same range of HRT (3–33 h), with an average of $36 \pm 13\%$ of the COD removal due to processes not associated with power generation (Figure 6). Power density decreased from 17 to 12 mW/m² over this range of HRTs. The Coulombic efficiency of the system ranged from 3 to 12%, indicating there was substantial COD that was not associated with power generation. While these Coulombic efficiencies are low, those reported by others have varied over a large range of 0.04–97% (5, 11, 16).

COD removal in the absence of power generation cannot be explained solely on the basis of oxygen transfer across the air-cathode. On the basis of values reported in Basura et al. (19), the oxygen flux through the membrane is estimated as

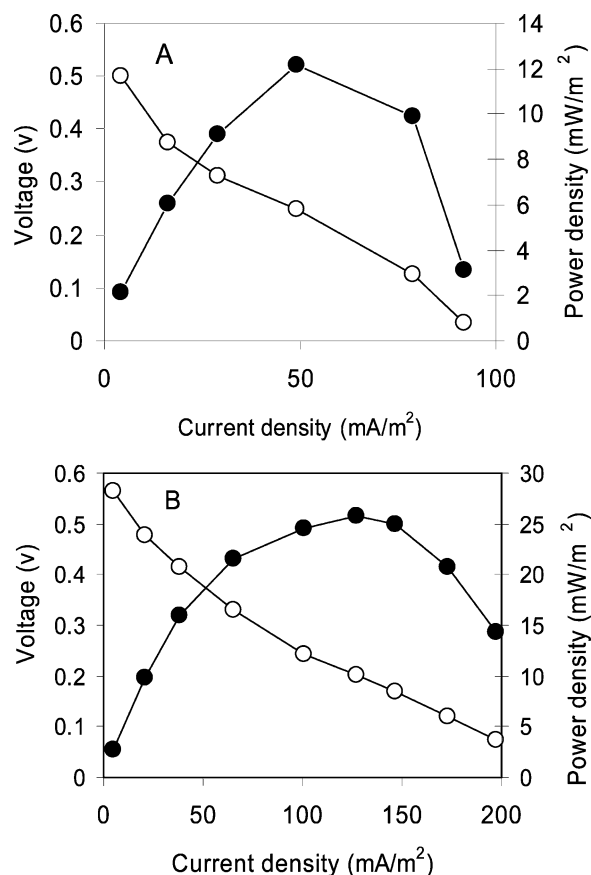


FIGURE 5. Voltage (○) and power (●) generated in the SCMFC when resistance (electrical load) on the system is changed from 16 to 5000 Ω . (A) HRT = 12 h, COD = 220 mg/L (cathode air flow rate = 5.5 L/min; reactor initially inoculated with *G. metallireducens*). (B) HRT = 6 h, COD = 210 mg/L (passive cathode air flow; wastewater inoculum only).

much as 2.3 mg/h. While this could achieve as much as 93% of the COD removal at the longest detention time (33 h), it could only produce a total of 9% of the COD removal at the 3 h HRT in Figure 6. There could have been a loss of COD using other electron acceptors (such as nitrate and sulfate) present in the wastewater. Biomass production could account for additional COD removal, but it was not possible to establish a complete mass balance of COD in this system.

Implications for Using MFCs for Wastewater Treatment.

Electricity was produced in a single-chamber MFC, but it was found that a large percentage of the organic matter in the wastewater was removed by processes that did not generate electricity. To increase the power density of the system, we will need to find ways to increase the fraction of the organic matter that is converted into electricity. However, the organic matter in wastewater is essentially free. As long as COD removal is accomplished, by electricity generation or other methods, the goal of wastewater treatment is achieved. It appears that substantial losses of COD here resulted from passive oxygen transport into the reactor by diffusion across the proton exchange membrane. COD reduction due to passive oxygen transfer may actually be beneficial when compared to the high cost of forced-air oxygen transfer using blowers in wastewater treatment systems such as activated sludge. Clearly, additional work will need to be done to better understand how electricity generation affects COD removal and how operational factors such as hydraulic retention time and air flow rate through the cathode can be optimized.

The capital cost of the SCMFC used here could be substantially reduced through system designs that use less

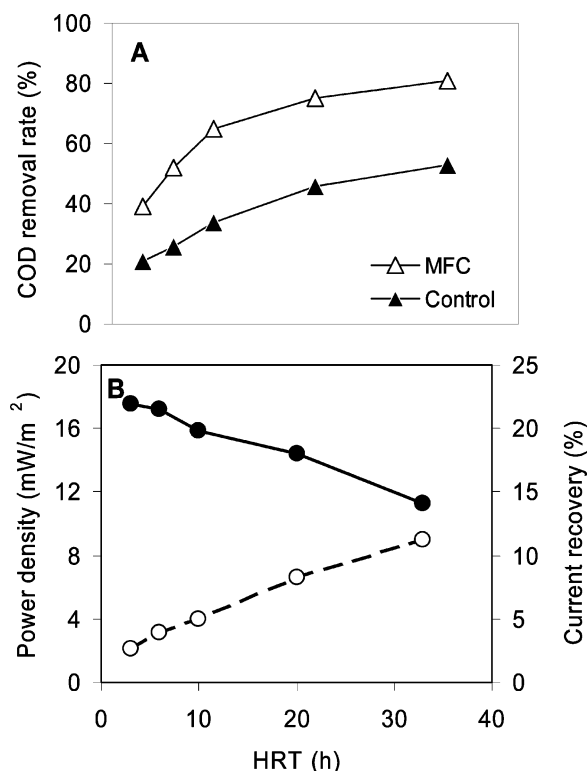


FIGURE 6. (A) COD removal rate in MFC (Δ) as compared to control reactor (\blacktriangle ; circuit disconnected). (B) Power density (\bullet) and current recovery (\circ) in MFC as a function of HRT (COD = 210 mg/L, 465 Ω).

expensive electrodes and membranes and that minimize catalyst content. Several reactor systems have used graphite rods as electrodes (5, 14, 18), but graphite felt or carbon cloth may provide less expensive alternatives (15). Other alternatives include conductive materials with coatings such as polyaniline that were recently shown to boost current densities in MFCs by more than an order of magnitude (24). Advances are also being made in membranes that may result in the replacement of the Nafion membrane used here with less expensive membranes (22).

Providing adequate sanitation and clean water to a global population is an economic challenge. Advanced wastewater treatment systems that are mandated by law in the U.S. to protect human health and the environment are too costly to be installed or operated and maintained in developing countries where the need for sanitation is greatest to protect human health and the global spread of disease. Even in the U.S., there are substantial economic challenges for maintaining the current levels of water and wastewater treatment. It is estimated that \$2 trillion is needed in the U.S. over the next 20 years for building, operating, and maintaining wastewater and drinking water facilities (1). About \$45 billion is needed for wastewater infrastructure improvements in addition to current annual costs of \$25 billion. Operating costs are a substantial factor in wastewater treatment, with over half of the operating expenditures typically needed for wastewater aeration. Power production measured here could provide much needed energy in the U.S. from domestic wastewater alone. Processes that can generate electricity during domestic and industrial treatment will help to reduce the economic burden of treatment and provide access to sanitation technologies throughout the world.

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Note Added after ASAP Posting

This paper was released ASAP on 02/21/2004 with an error in the second line of the Introduction. The correct version was posted on 03/03/2004.

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