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Review

A new future for carbohydrate fuel cells

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ABSTRACT

The development of renewable energy sources to reduce our dependence on limiting fossil fuel reserves continues to be a critical research initiative. Utilizing the abundant high energy content of carbohydrates contained in biomass (cellulose and hemicellulose) must be considered to be an important contribution to our overall energy budget. Carbohydrate-derived furan-based liquid fuels and especially ethanol are becoming important added components forming gasoline blends to lower overall fossil fuel use. Alternate renewable energy processes that more efficiently use the carbohydrate energy content are desirable and would lower the overall carbohydrate input requirement for energy production. Recently, new catalysts have shown the feasibility of efficiently transporting the 24 electrons in glucose to fuel cell electrodes making possible the direct conversion of the stored energy in carbohydrates into electricity with the benign formation of carbonate and water as products. The conversion of glycerol, a byproduct of biodiesel production, into three-carbon carbohydrates provides another opportunity to produce electricity from an abundant carbohydrate source. New developments in catalyst systems promise to make carbohydrate fuel cells an important part of future energy strategies.

1. Introduction

The United States in particular and the world in general, do not suffer from a shortage of energy. The problem has been our narrow historical focus on using the convenient but finite reserves of fossil fuels on an ever-larger scale to meet our increasing industrial and transportation energy needs. Energy shortages arose in the 1970s when petroleum-based products became in short supply due to market limitations, thereby interrupting and temporarily slowing worldwide commerce. From these initial events, petroleum-supply problems have continued on an almost decade-by-decade time frame and the urgency to develop the earth's other ample resources is now fully recognized.

The enormous scale of current fossil fuel use is now associated with climate problems, environmental degradation, and geopolitical problems, which in turn create market instability and greater competition for remaining fossil fuel reserves [1–3]. The recent catastrophic crisis in the nuclear power industry in Japan and its worldwide repercussions threaten to decrease energy production from this important, reliable and well-integrated energy source and adds impetus to the need to develop alternative energy sources.

The emerging energy contributions from wind farms, photovoltaic cells for direct electricity production, and other ongoing uses of solar energy are making important contribution to our overall energy demands and will become more important as technical developments lower costs and improve efficiency. However, these processes currently suffer from limited scale and intermittency, which results when there is no energy production on windless and overcast days and especially at nighttime, when solar energy is absent. These latter problems require the development of large, convenient and low-cost methods to store excess electrical energy when resources are available, and releasing it when they are not [4].

The development of new energy sources requires that new technologies be developed to exploit them. The important question then becomes "What abundant, renewable and sustainable energy resource is available on the enormous scale needed to replace the vast and reliable, but dwindling, fossil fuel reserves"?

Biomass has the potential to become both a viable short- and long-term resource to replace fossil fuels during the transition from fossil fuel use to alternative energy sources [5,6]. Biomass is an extensive and almost endlessly renewable resource that is formed daily by converting CO_2 and H_2O into stable and harvestable, high-energy organic molecules through photosynthesis. This natural process represents a large, stable "storable source" of solar energy. Glucose and other carbohydrates, in the form of free sugars, cellulose and hemi cellulose, account for up to 70% of the organic

Abbreviations: MV, oxidized methyl viologen (1, 1′-dimethyl-4,4′-bipyridine); MVr, reduced methyl viologen; MMV, monomethyl viologen; SHE, standard hydrogen electrode; Wh/kg, Watt-hours/kilogram.

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content of biomass [7,8]. Glucose and other hexoses (six carbon carbohydrates) have a high-energy content of 4420 Wh/kg and the still plentiful pentoses, tetroses, and trioses have abundant but proportionately less energy. Biomass is therefore a resource that rivals fossil fuels on the enormous scale available that is capable of providing the appropriate high-energy content that is needed to meet present and predicted energy needs [5–8]. Given this potential for providing large scale energy for societies needs, what process or processes are the most advantageous to exploit this resource in a sustainable manner?

The possibility of using carbohydrates from biomass for transportation energy and for electrical energy production has been considered for decades [5–8]. Although progress is being made in several areas of renewable energy there remains a need for further effective and low-cost catalyst systems to be developed to carry out the complex chemical and/or electrochemical conversions required. However, this important objective continues to attract interest and stimulate efforts toward its development. Two general research efforts have been and are being actively explored for converting the energy content of carbohydrates into convenient energy sources to meet society's needs.

2. Transportation fuels

The direct formation of high-energy liquid fuels from carbohydrates with sufficient energy content, volatility, and stability for safe use in internal combustion engines is a promising research objective to supplement or replace gasoline as a transportation fuel. Preliminary and important steps have been taken and processes have been reported that produce high-energy, furan-based liquid fuels [9–11]. Conversion efficiencies of ~ 50–80% have been reported, and overall useful fuels are emerging. While promising, better catalysts and more efficient second-generation processes are needed to increase efficiency, produce greater volume, and lower costs to more competitive levels.

Ethanol production now accounts for 90% of carbohydrate-derived liquid fuels and is used to supplement or even replace current petroleum-based fuels [12,13]. However, more than 50% of the original energy content of glucose is lost during the conversion to and separation of ethanol from the dilute fermentation mixture [12,13]. Until glucose and other carbohydrates are easily separated from the cellulosic and hemi cellulosic content of biomass and efficiently utilized, the production of ethanol will likely continue to require subsidies and rely on agriculturally-derived sugars and starches that compete with food supplies.

The previous discussion regarding liquid fuels has presented the possibility, desirability and promise of large-scale energy production of liquid transportation fuels from energy rich and renewable carbohydrates derived from biomass. However, even if this objective is successful, the inefficient utilization of the initial energy content of the parent carbohydrate remains an important problem. This has been documented for ethanol use, where only 10–15% of the original carbohydrate energy content is actually utilized in vehicle propulsion [14]. An important recent assessment of bioenergy use concludes [14–16] that using biomass to power electric automobiles is three times more efficient and more environmental compatible than using ethanol for this purpose. More efficient energy use of the initial carbohydrate energy content is clearly desirable and when achieved will actually lower the amount of carbohydrate resources needed.

Carbohydrates have not been used for electrical energy production because effective and low-cost catalyst systems have not been developed to carry out the required complex electrochemical conversions. However, this important objective continues to attract interest and to stimulate efforts toward its development [17,18]. Unfortunately, up to the present time, only very low electrical power production has been reported. The prospect of deriving electrical energy directly from carbohydrates is important and is the focus of the remaining discussion.

3. Electrical power from carbohydrate fuel cells

How is electricity produced from carbohydrates? One approach is to blend biomass at 15% or more with coal in coal-fired power plants [15,16]. While this approach is feasible, decreases coal use and lowers overall greenhouse gas emissions, it is not the most efficient use of carbohydrate energy. A more promising approach was reported more than 60 years ago when electricity was produced from glucose using a simple Pt-based fuel cell [6].

A fuel cell is an electrochemical device that catalytically removes electrons from an energy-rich fuel source at one electrode compartment (the anode) and transfers them to a second electrode compartment (the cathode), where they combine with an oxidizer, which is typically oxygen [17]. Fig. 1 shows this process in the form of a schematic diagram. The combination of two half-cell reactions produces a cell voltage equivalent to the sum of the two half-cell potentials and generates an electrical current in the external circuit. The two half-cell reactions for glucose and oxygen (Reactions 1–2, pH 12) show that oxidation of the glucose fuel by oxygen produces a cell voltage of 1.45 V. Catalysts for both half-cell reactions are critical for smooth and efficient fuel-cell operation [17,18].

$$\text{Anodic Reaction } C_6H_{12}O_6 + 36\,OH^- = 6CO_3^{2-} + 24\,H_2O + 24\,e \quad E = 0.93\,V \tag{1}$$

$$\text{Cathodic Reaction } 6O_2 + 24\,e + 12\,H_2O = 24\,OH^- \quad E = 0.52\,V \tag{2}$$

$$\text{Overall Reaction } C_6H_{12}O_6 + 6O_2 + 12\,OH^- = 6CO_3^{2-} + 12\,H_2O \quad E = 1.45\,V \tag{3}$$

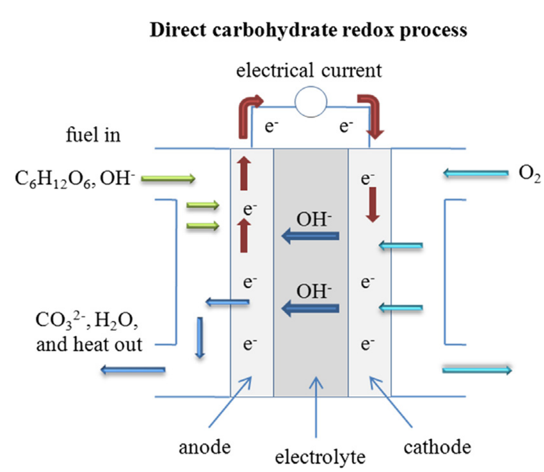

Fig. 1. Schematic representation of a carbohydrate fuel cell. The anode compartment on the left receives the carbohydrate fuel to be oxidized. This compartment contains the viologen catalyst in contact with the anodic current collecting electrode. The cathodic compartment on the right receives electrons removed from the fuel and catalytically transfers them to oxygen forming OH^-. The semi-permeable membrane separating the electrochemical compartments allows for transfer of OH^- to facilitate reaction and maintain ionic balance.