Biomass Power Generation Using Liquid Tin Anode SOFC

J. Bentley, T. Tao and M. Koslowske
CellTech Power LLC, Westborough MA, USA jbentley @ celltechpower.com

ABSTRACT

Currently biomass contributes only 1% of U.S. electric power despite available resources to provide over 20%. Barriers to increased use of biopower include low efficiency of current generators, high capital cost, low fuel energy, feedstock variability and the inability to scale to small power ranges. In a carbon constrained world, increased use of biopower can simultaneously address energy independence and climate change drivers while providing economic growth. Increased biomass utilization in the power sector will enhance energy security, create jobs and enables a net-negative CO_2 process. The Liquid Tin Anode Solid Oxide Fuel Cell (LTA-SOFC) is a transformational technology that addresses these barriers by simple, highly efficient, direct conversion of biomass to electricity. Direct biomass and fossil fuel power generation has been proven in the LTA-SOFC at the single cell level with demonstrated efficiencies as high as 55%. System level analysis has projected biomass powerplant efficiency of over 50%. LTA-SOFC Direct Biomass will deliver all of the renewable benefits of biomass while reducing emissions and feedstock usage by 2-3X. LTA-SOFC technology is also scalable for high value portable power applications using diesel and other sulfur bearing hydrocarbons.

Keywords: biomass, biopower, fuel cell, renewable energy, solid oxide

1 OVERVIEW

The Liquid Tin Anode Solid Oxide Fuel Cell (LTA-SOFC) provides a potential pathway to improve the efficiency and capital cost of biomass power and also enable smaller scale applications of biopower. Recently a technical program was undetaken at CellTech to demosntrate the feasibility of direct biomass conversion, using biomass feed stocks which can have significant societal, environmental and economic impacts. This involved study of the behavior of biomass ash while undergoing in situ gasification in the anode section of the cell. Conventional biomass combustion plants typically require extra care to avoid slagging of ash with low melting temperatures. CellTech addressed this issue head-on by operating several different types of biomass in an actual LTA-SOFC cell. Poplar, switchgrass and corncob biochar, representing the spectrum of potential biomass feedstocks, were used as fuel. Post-test analysis indicated no ash fusion and near 100% fuel utilization (little residual carbon left). SEM-EDAX analysis showed that the basic biomass plant structure survived the conversion process with limited signs of melting that could impair ash removal and fuel consumption. EDAX analysis of the chemistry of ash residual from LTA-SOFC operation indicated that potassium, the key element in biomass partially responsible for slagging was greatly reduced compared with potassium levels shown in combustion ash samples. This finding demonstrates the feasibility of direct biomass to power in LTA-SOFC by removing ash fusion as a perceived roadblock. Along with the demonstration of near 100% fuel utilization of biomass early research has achieved all of its stated objectives. The next step includes an effort which will address biomass fuel efficiency in a continuous feeding. These findings provide confidence that co-development of biopower applications of LTA-SOFC can occur in parallel with other LTA-SOFC applications, such as portable power, providing a broad technological underpinning for commercialization of this breakthrough technology.

1.1 Significance of Improved Biomass Power Conversion Technology

In a carbon constrained world, increased use of renewable biomass power can simultaneously address energy independence and climate change while providing economic growth for the USA. Barriers to increased use of biomass for electric power include low efficiency of current generators, high capital and fuel transportation costs, low fuel energy, feedstock variability and the inability to scale to small power ranges. These factors all drive up the cost of biomass power compared to conventional sources. High cost is the main road block to broad usage of biomass. Currently biomass contributes only 1% of U.S. electric power despite available resources to provide over 20%. The LTA-SOFC is a transformational technology that addresses cost barriers by simple, direct conversion of biomass to electricity with projected efficiency of twice that of conventional biomass generators- reducing fuel cost by half. LTA-SOFC has shown good laboratory performance and life on fuels such as natural gas and military JP-8. Biomass has not been studied in detail until recently. A perceived key issue prior to this effort has been that some types of biomass contain considerably more ash as well as potentially troublesome elements which may cause ash melting that interferes with fuel cell operation.

2 LTA-SOFC BACKGROUND

The LTA-SOFC is an advanced fuel cell with the demonstrated capability of efficiently and directly generating electrical power from fuels such as biomass, diesel, natural gas and coal with no fuel reforming. Direct carbonaceous fuel conversion in a fuel cell is a transformational concept because of the simplicity and efficiency that is gained by converting common fuels into

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electrical power in a single electrochemical process. Technical issues specific to the use of biomass have been be identified and potential mitigation strategies proposed. Successful adaptation of the LTA-SOFC for biomass operation will allow this transformational technology to be commercialized in power ranges from low kilowatt to multi-megawatt range.

2.1 Tin Anode Electrochemistry

Tin is a metallic element with unsaturated p-electrons. It has a very low melting point (mp 232° C) but an exceptionally high boiling point (bp 2,602° C). The chemical reaction of tin with oxygen is exothermic and spontaneous as shown in Equation (1). The electrochemical reaction between tin and air using oxygen transporting membranes, such as the solid oxide ceramic YSZ, at 1,000°C is given in Equation (2).

$Sn\ (l) + O_2\ (g) = SnO_2$ $\Delta G = -74.3$ kcal/mole [1]
$\Delta E = -136.5$ kcal/mole

$Sn\ (l) + 2O(2e-) = SnO_2 + 4e-$ OCV = 0.78V [2]

At the anode, tin combines with oxygen ions to form tin oxide and produces an Open Circuit Voltage of 0.78 volt with an ambient air cathode. Tin is a reactive and consumable anode similar to a battery anode. In order to maintain power production, fuel is introduced to reduce the tin oxide back to tin. Equations (3) to (6) show reduction pathways for SnO_2 with hydrogen and carbon, which are the major constituents in biomass, and CO, an intermediate product, to form tin, at standard pressure and 1,000° C. All these reduction reactions are spontaneous as shown by their negative free energies.

$SnO_2 + 2H_2(g) = Sn(l) + 2H_2O(g)$ $\Delta G = -10.5$ kcal/m [3]

$SnO_2 + 2C = Sn(l) + 2CO(g)$ ΔG -32.8 kcal/mole [4]

$SnO_2 + C = Sn(l) + CO_2(g)$ ΔG=-20.3kcal/mole [5]

$SnO_2 + 2CO(g) = Sn(l) + 2CO_2(g)$ ΔG= -7.9 kcal/mole [6]

The equations indicate that in the presence of fuel molecules, such as hydrogen, carbon, CO or any hydrocarbon that is readily thermally decomposed in situ, formation of tin oxide can be reversed. The net result of combining equations (2) to (6), is that electricity is produced in a way as if a direct oxidation of the fuel molecules occurs, in other word, LTA-SOFC acts like a "direct biomass" conversion fuel cell. Experimental validation of the ability of LTA-SOFC operation on carbon was established in 1999 when the first generation design was operated on coal. Figure 1 shows the overall reactions of an LTA-SOFC cell. Figure 2 shows the various chemical and electrochemical reactions involved in gasifying fuel and converting it to electrical energy. LTA-SOFC has been under development for over 10 years, primarily at CellTech Power. In that time, CellTech has significantly advanced LTA-SOFC technology and achieved a number of fundamental breakthroughs. One important milestone in 2004 was the demonstration of a complete 1 kW standalone LTA-SOFC fuel cell system operating on natural gas (Figure 3).

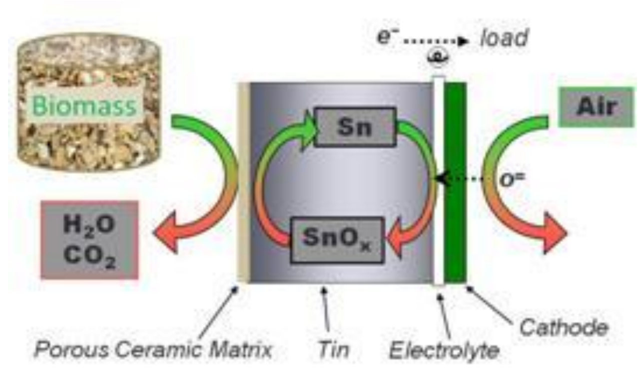

Figure 1: The Liquid Tin Anode oxidizes carbonaceous fuels to directly create power. The porous ceramic matrix separator is a CellTech invention which contains the tin while allowing fuel-tin oxide reactions.

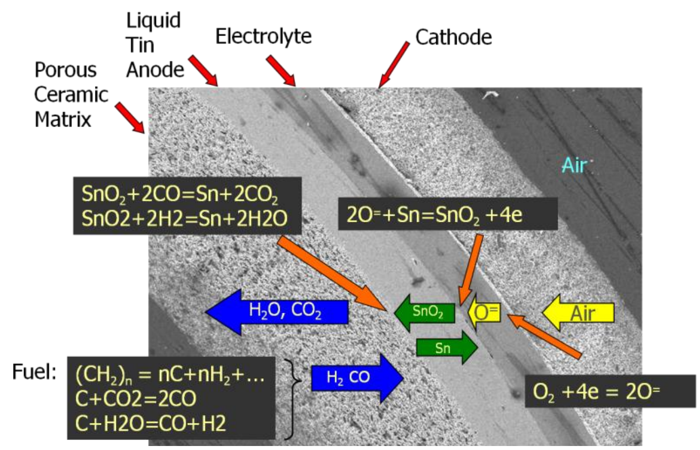

Figure 2: Equations for chemical/electrochemical reaction in LTA-SOFC superimposed on an SEM cross-section.

Another CellTech breakthrough, accomplished in 2006 in a DARPA funded program was the demonstration of the world's first and only direct JP-8 fuel cell. The US Army has called the capability of a fuel cell to operate on JP-8 the "Holy Grail" of military power systems. Efficient conversion of biomass including wood, biochar and biodiesel has been demonstrated for short periods of time in the LTA-SOFC at the single cell level.

The LTA-SOFC is closely related to SOFC technology, using the same cathode and electrolyte materials while replacing the conventional solid nickel cermet anode with molten tin as shown in Figure 1. This new anode material allows the direct conversion (no reformer or gasifier) of carbonaceous fuels containing carbon, oxygen and hydrogen. The LTA-SOFC is capable of using fuels in any state- gaseous, liquid or solid. The Gen 3 is a tubular design with an external anode. The tin anode is contained in a thin layer by a "breathable" porous ceramic matrix which allows

Figure 3 - Earlier generations of LTA-SOFC were integrated into a 1 kW prototype operating on natural gas.

transport of gaseous fuel components to the surface of the tin anode and allows reaction products (water and CO_2) to be transported away. All Gen 3 LTA-SOFC cells share a common anode chamber, thus allowing direct introduction of liquid or solid fuel into the chamber, direct electricity generation through an in situ gasification.

2.2 Biomass Applications of LTA-SOFC

Solid fuel does not need to be in direct contact with the cell since the cell reaction products (CO_2 and H_2O) create an in situ gasification environment as shown in Figure 2. The in situ gasification concept has been validated using solids such as solid carbon, bio-derived charcoal packed around a Gen 3. The cell was operated until all or a large portion of the fuel was consumed.

Early LTA-SOFC development utilized hydrogen and natural gas which does not form residue or ash. The 1 kW prototype shown in Figure 3 was operated on NG for over 2000 hours illustrating some technical maturity of LTA-SOFC. JP-8, diesel and other petroleum products have a minute amount of non-combustible solid material that does not exceed around 0.02 mass percent so for the useful life span of thousands hours involved in portable power applications build-up of ash or carbon has not been a major concern. More recently CellTech's analytical and experimental work has expanded to include coal, which can indeed have high ash content and long operating life requirements. However, the current operational concepts for using coal in the LTA-SOFC at the scale of 200 MW and above a Tin/Coal Reactor (TCR) may be preferred to the in situ gasification. In this scheme, coal is reacted with tin oxide in the TCR and ash is gravimetrically separated from the tin. For biomass applications, with power ranges from single digit kW to no more than 20MW the in situ gasification may be more advantageous than the TCR. In this configuration biomass will be introduced directly to the LTA-SOFC cell anode chamber and residual ash will be in direct proximity to cells with porous separators similar in design to the Gen 3.1. Operation of a biomass generator in this mode requires a solution to issues related to biomass ash formation.

The Liquid Tin Anode Solid Oxide Fuel Cell (LTA-SOFC) provides a potential pathway to dramatically improve the efficiency and capital cost of biomass power. As a first step, recent work studied the behavior of biomass ash while undergoing in situ gasification in the anode section of the cell. Conventional biomass combustion plants typically require extra care to avoid slagging of ash with low melting temperatures. CellTech has addressed this risk head-on by operating several different types of biomass to produce useful power in an actual LTA-SOFC cell. Poplar, switchgrass and corncob biochar, representing the spectrum of potential biomass feedstocks, were used as fuel. Post-test analysis indicated no ash fusion and near 100% fuel utilization (little residual carbon left). SEM-EDAX analysis showed that the basic biomass plant structure survived the fuel cell power generation process with limited signs of melting that could impair ash removal and fuel consumption. EDAX analysis of the chemistry of ash residual from LTA-SOFC operation indicated that potassium, the key element in biomass responsible for slagging was greatly reduced compared with potassium levels shown in combustion ash samples. This finding demonstrates the feasibility of direct biomass to power in LTA-SOFC by removing ash fusion as a perceived roadblock. Successful conversion of biomass in a small LTA-SOFC cell also supports the exciting possibility of small scale (1 to 10 kW) biopower generators, a market that conventional biopower technology cannot address.

2.3 Future Biomass Work

Recent biomass work has achieved all technical objectives and successfully demonstrated a wide spectrum of biomass for direct conversion to electricity in a LTA-SOFC. However early testing was conducted in a batch mode and therefore focused on the non-volatile parts of biomass including char and ash. It was not able to address power production from the volatiles component of biomass which contains substantial fuel value. The results support continued development of biomass to power in LTA-SOFC including an effort to address biomass fuel efficiency in a continuous feeding test allowing utilization of biomass volatiles. These early findings provide confidence that co-development of biopower applications of LTA-SOFC can occur in parallel with other LTA-SOFC applications, such as portable power, providing a broad technological underpinning for commercialization of this breakthrough technology.

3 CELLTECH'S MARKET STRATEGY

The Liquid Tin Anode Solid Oxide Fuel Cell (LTA-SOFC) turns common fuels like biomass and diesel into electrical power with projected efficiency of up to 60%. LTA-SOFC is dramatically different from hydrogen fuel cells because it operates on readily available, low cost fuels with no fuel processing, greatly reducing system complexity and cost. This innovative, one-step process from fuel to electricity replaces inefficient combustion and gasification based generation. Additionally, it resists sulfur and carbon- which are poisons to conventional fuel cells. The market opportunity for LTA-SOFC is staggering because this techology platform addresses military and commercial markets ranging from 20 Watt portable power units to 500 megawatt coal baseload generators. CellTech's market approach begins with Mobile Energy niche markets including early sales to military customers. Biomass power is a midterm market which could develop into a potential market of $50 Billion annually in the US alone.

3.1 Market Opportunity

CellTech's first market is Mobile Energy Figure 4 a $6 Billion market where convenience and need drive higher allowable costs and lower lifetime requirements than

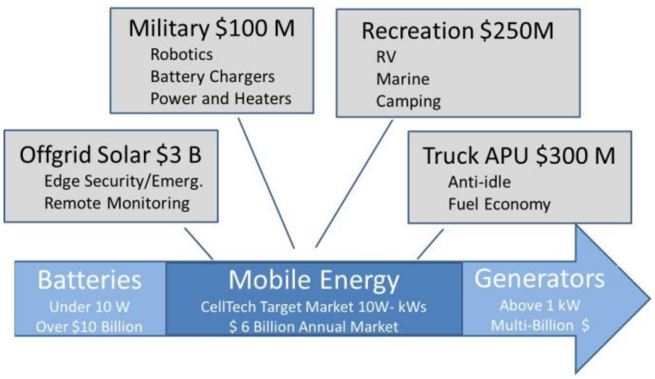

Figure 4 - CellTech has targeted the $6 Billion/yr Mobile Energy Market as the entry point for LTA-SOFC technology. This market provides a platform for entry into biopower as a mid-term market.

stationary applications. This market encompasses many off-grid markets where electricity is not priced as a commodity including traditional portable power as well as Auxiliary Power Units for recreation and transportation. Frost and Sullivan defines the Portable Power market more narrowly as engine generators between 1 and 17 kW with annual sales of $782 M in 2008 The military is the lead Mobile Energy niche because of strong tactical and strategic drivers. Operationally, more efficient field generators are required because of the cost (at least $15/gallon and greater when delivered to front lines) and casualties associated with fuel delivery convoys. Recognizing the strategic threats of reduced fossil fuel availability and global warming Defense Secretary Robert M. Gates has identified energy as one of the US military's top "transformational priorities." This means the military will require more efficient generators and greater reliance on renewables like biomass .

CellTech's business strategy is to manufacture LTA-SOFC Modules for sale to integrators in a range of military and commercial power generation markets.

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