INTRODUCTION OF LIQUID ANODE/SOLID OXIDE ELECTROLYTE FUEL CELL AND ITS DIRECT ENERGY CONVERSION USING WASTE PLASTICS

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ABSTRACT

Liquid anode fuel cell/battery device is a modified version of SOFC. It operates at temperatures of 700°C to 1000°C. Its electrolyte and cathode are made of typical SOFC components such as stabilized zirconia (Ca, Mg, Y, Ce and Sc, etc.) and lanthanum manganite (doped with calcium and strontium). However its anode is made of molten p-orbital-electron metals such as bismuth, indium, tin and antimony. The device is a battery itself and it can produce electricity by oxidizing its liquid anode directly without an addition of fuel. The device is a fuel cell also when fuels such as hydrogen, hydrocarbons, carbon and sulfur, etc. are introduced and these fuels can be directly converted to electricity without a need of reforming. Since its invention in 1997, prototypes of kilowatts class liquid anode fuel cell/battery have been made and one had run continuously for more than 2000 hours using hydrogen and natural gas. Fuel efficiencies with carbon, polystyrene, polyethylene and polypropylene as fuels were found to be 45-62%, 48%, 45% and 45% respectively in a single liquid anode cell.

INTRODUCTION

An Overview of Direct Carbon Conversion

Direct common fuel (carbonaceous based) to energy conversion, especially direct carbon conversion, had historically drawn significant attention. During 19th century when coal was a major source of energy, coal-firing electricity generators had very low fuel efficiency, merely 3-7%. Many well known scientists and inventors, Benjamin Franklin, Wilhelm Ostwald (1) and Edison (2) had involved, proposed or experimented with ideas of direct conversion of carbon to electricity. It was an American inventor W. W. Jacques (3) who more than 100 years ago first made a 1 kW direct carbon battery using molten potassium or sodium hydroxide as electrolyte. Unfortunately the expensive potassium hydroxide electrolyte was converted to carbonate during process. Later attempts focused on replacing hydroxides with molten alkali carbonates. One notable example was a Swiss chemist Emil Baur (4) who dedicated 30 years to systematically study direct carbonaceous fuel conversion. His efforts plus many others eventually led to the birth of modern molten carbonate fuel cells.
Efforts of direct carbon conversion with a liquid or molten electrolyte had never ceased. M. Anbar and R. D. Weaver et al. (5) of Stanford Research Institute attempted a molten carbonate electrolyte combined with lead/lead oxide. More recently, researchers at Scientific Application & Research Associates, Inc. (SARA) (6) modified the W. W. Jacques invention and they claimed, by using a hydroxide selected from a group consisting of aluminum, calcium, cesium, potassium, sodium, rubidium and strontium, that they were able to overcome carbonate problem. Scientists led by John Cooper at Lawrence Livermore National Lab (7) used reactive carbon particles mixed with alkali metal carbonates combined with a molten carbonate electrolyte. However, in the Cooper’s device, only highly reactive nano-particle carbon was used.

Common carbon such as graphite or coal is relatively stable; its oxidation requires active chemical promoters or catalysts such as alkali hydroxides or higher temperatures. Zirconia based solid electrolytes operating at temperatures of 800-1000°C were attempted by Thomas Tao during 1994-1998 (8) for direct conversion of carbon. He placed an electrically conductive carbon such as a graphite rod and conductive carbon powder directly onto the surface of an yttria stabilized zirconia. However, lost contacts between graphite and the solid electrolyte made it impossible to achieve a steady and useful electric power.

One interesting attempt was to gasify carbon or coal in situ of a solid electrolyte fuel cell. Gür et al (9) placed coal particulates inside a platinum pasted solid oxide fuel cell, not in direct contact with either an electrode or an electrolyte. Carbon dioxide produced reacted with coal to form carbon monoxide in situ. It was carbon monoxide gas being oxidized at the Pt electrode, and the net result was a continuous consumption of coal. However, the Pt electrode was simply too expensive for any practical use.

Other interesting attempts worth mentioning included dissolution of carbon in a molten iron anodic media. Researchers at GE (10) in 1950s and 1960s had experimented with a molten iron bath encased in a calcium stabilized zirconia (as electrolyte) container for direct conversion of carbon and carbonaceous fuels. Later a few researchers around the world continued this effort (11). I. Yentekakis et al in 1989 built a kinetic model (12) for the Fe-C system. At carbon concentration of 4.26 wt%, the Fe-C formed an eutectic point of 1153°C degree that was 380°C degree lower than the pure Fe melting point. In theory, the molten iron-carbon system had to operate at temperatures much higher than 1000°C but somewhat lower than 1533°C. Such an ultra high temperature fuel cell is still waiting for material science to catch up. A similar attempt by H. Yokokawa et al. in 1994 (13) was to replace anode electrode with metal carbides. Vanadium, tungsten and zirconium carbides or these carbides mixed with carbon were used as anodes and as fuels. However their detrimental impact on zirconia electrolyte made such devices practically useless.

With predicted fuel efficiency as high as 80% [John Cooper (7)] and abundant coal, biomass and recyclables/wastes, importance of direct fuel (carbon) conversion has long been recognized. For instance, military plastic packaging waste consists of predominately polyethylene, polypropylene and polystyrene, and their direct energy conversion in the field not only reduces waste to be disposed of but also provides electricity.

This paper focuses on the work of direct fuel conversion in single liquid anode fuel cells using plastics. Some work on wood and carbon is also discussed.
**Liquid Anode Fuel Cell/Battery**

In 1997 (Tao) Thomas Tao et al (14) invented a liquid anode/solid electrolyte fuel cell/battery for direct carbon conversion. A 2-cell-stack was built and tested as shown in Fig 1. This tubular-cell stack had a size of an AA-sized battery. Carbon fuels including Cabot & Tilcom carbon and graphite powder and rods were literally inserted into the hot liquid anode through an opening. The carbon fuel was mixed and in direct contact with the liquid anode. This stack produced a continuous electric power of about 1 watt for two weeks. 1.5 Volt flash light bulbs were used as a load. Raw coal pellets obtained from a local Rhode Island coal distributor were charged into the stack also.

In 2004, two prototypes of kilowatt liquid anode fuel cell/battery system were made as shown in Fig 2. Part of the work has been described in a number of patents and applications (Thomas Tao, et al.) (15). They were designed for use of gaseous fuels such as hydrogen and natural gas and the first such unit ran continuously for more than 2000 hours in alternation of standing-by mode, battery mode and fuel cell mode.

**THEORY – CHEMISTRY OF P-ORBITAL ELECTRON METALS**

Metals containing unsaturated or unpaired p-orbital electrons have unique physical and chemical properties. This group of metals (Ga, In, Sn, Sb, Tl, Pb, Bi and Po) has low melting points, well below 1000°C. Their oxidation reactions are spontaneous and exothermic. OCV of oxidation reactions of Sb, Sn, In and C, CO, H2 are shown in Fig 3.

In general, OCV of a metal oxidation decreases as temperature increases. For instance, 2In + 3/2 O2 = In2O3, at ambient temperature its OCV is 1.45 V and reduces to 0.85 V at 1000°C degree. However carbon is an exception: for C + O2 = CO2, its Gibbs Energy (ΔG) and its OCV (1.02 V) have little to do with temperature as shown in a flat line in Fig 3; for 2C + O2 = 2CO, its OCV actually increases as temperature increases. This implies that any metal oxide thermodynamically can be reduced back to metal by carbon at a proper temperature (a threshold). For Sb, Sn and In, the threshold temperatures (at standard conditions) are 410°C, 650°C and 750°C respectively.

Hydrogen oxidation is similar to that of a metal, but its OCV is less sensitive to temperature as shown in a less steep slope in Fig. 3. Similar to carbon, there are temperature thresholds for hydrogen also. These temperatures for Sb, Sn and In are less than 0°C, 600°C and 900°C respectively.

The liquid anode’s battery function comes from a direct oxidation of the metal. To illustrate let’s take Sn as an example as shown in Eq (1), at 1000°C,

\[
\text{Sn(l)} + 2 \text{O}^{2-} = \text{SnO}_2 (s) + 4 \text{e}^{-} \quad \Delta G = -74 \text{ kcal/mol} \tag{1}
\]

where the Gibbs Energy of -74 kcal/mol gives an equivalent OCV of 0.8 volt, and l and s in parenthesis stand for a liquid and a solid state respectively.

The liquid anode fuel cell/battery has also been demonstrated to being electrically rechargeable. Electrically recharging is a reduction reaction by reversing direction of an
electrical current. Oxygen ions in anode are driven out by an applied electric field through electrolyte, releasing at cathode. This is identical to an electrically rechargeable battery such as Ni/Cd. Taking Sn as an example, the recharging reaction is

$$\text{SnO}_2(\text{a}) + 4e^- = \text{Sn}(l) + 2\text{O}^2-$$ outside field 0.81 – 1.2 Volt \[2\]

where a in parenthesis stands for SnO2 activity in liquid tin anode. It is worth mentioning that a liquid anode cell can be charged to an OCV higher than equilibrium (0.8 V) as shown in Eq (1), because its oxide activity can be less than one when unsaturated.

The liquid anode’s ability to be charged by carbonaceous fuel is shown in Fig 3 and subsequent equations [3] to [7]. Chemically (fuel) recharging is a reduction reaction, using fuel to reduce metal oxides to metals. In fact, fuel not only includes all carbonaceous such as charcoal, wood, paper, plastics and hydrogen, but also those containing nitrogen and sulfur as shown in equations [8] and [9]. Taking Sn as an example, simplified fuel reduction reactions are, at 1000°C:

$$\text{SnO}_2(s) + 2\text{C} = 2\text{CO}(g) + \text{Sn} \quad \Delta G = -33 \text{ kcal/mol} \ [3]$$
$$\text{SnO}_2(s) + \text{C} = 2\text{CO}_2(g) + \text{Sn} \quad \Delta G = -20 \text{ kcal/mol} \ [4]$$
$$\text{SnO}_2(s) + \text{CO}(g) = \text{CO}_2(g) + \text{Sn} \quad \Delta G = -8 \text{ kcal/mol} \ [5]$$
$$\text{SnO}_2(s) + 2\text{H}_2(g) = 2\text{H}_2\text{O}(g) + \text{Sn} \quad \Delta G = -10 \text{ kcal/mol} \ [6]$$
$$\text{SnO}_2(s) + \text{C}_n\text{H}_{2n+2} = 2\frac{(n+1)(3n+1)}{3n+1}\text{H}_2\text{O}(g) + 2\frac{n}{3n+1}\text{CO}_2(g) + \text{Sn}$$
$$\Delta G = -(21-33)\text{kcal/mol} \ [7]$$
$$\text{SnO}_2(s) + 1.33\text{NH}_3(g) = 2\text{H}_2\text{O}(g) + 0.67\text{N}_2 + \text{Sn} \quad \Delta G = -40 \text{ kcal/mol} \ [8]$$
$$\text{SnO}_2(s) + \text{S}(g) = \text{SO}_2(g) + \text{Sn} \quad \Delta G = -24 \text{ kcal/mol} \ [9]$$

These fuel reductions, Eqs [3] to [9], are thermodynamically favorable and spontaneous as evidenced by their negative Gibbs Energy. Eq. (7) using hydrocarbons as fuel is more complicated than the simplified equation itself because of thermal decomposition when exposed to a hot liquid anode. Plastics such as polyethylene and polypropylene are pure hydrocarbons and they break down to smaller species such as hydrogen, carbon and methane, etc at elevated temperatures.

Besides its multi-fuel capabilities, the liquid anode fuel cell has a battery function that tolerates a temporary interruption of fuel supply, can be engineered to provide substantially higher peak (surge) power and operates without an external battery pack as demonstrated in kilowatts prototypes shown in Fig 2 (the right unit).

Besides widely known cathode and electrolyte polarizations found in traditional SOFCs, the liquid anode has its unique anodic polarizations when it operates in fuel cell mode: they can be suggestively divided into two main groups. The first is related to reaction kinetics, i.e. activation energy of fuel reaction with metal oxides. The second includes diffusion and transfer of species at the fuel/liquid anode interface and within the bulk of
the liquid anode. These species include fuel molecules (H₂, CO, C, etc.), anodic metal oxides (SnO, SnO₂, In₂O₃, Sb₂O₅, Sb₂O₃ etc.) and reaction products (water, CO, CO₂ etc.). Preliminary data also indicated that oxygen transfer from electrolyte to the liquid anode was not a limiting factor at current densities less than 0.5 amp/cm².

When a liquid anode device operates in battery mode, it results in formation of metal oxides. Its battery performance depends on the liquid anode, its type and amount. It also relates to oxygen solubility and diffusivity in the liquid anode, ionic and electronic conductivities of anodic metal oxides and interaction of zirconia electrolyte with anodic oxides.

**EXPERIMENTAL**

At left in Fig 4 is a CAD drawing of an actual liquid anode cell with a standard configuration. In this configuration the liquid anode was inside the electrolyte tube. The cell had an active length of 15 cm and a diameter of 1.75 cm. Its electrolyte was made of 8YSZ and its cathode made of doped La manganite. Pt wires were used as cathode current collector. Direct plastic addition was conducted by gravity feed, manually dropping plastic pellets of polystyrene (PS), polypropylene (PP) and polyethylene (PE) through a fuel feed tube into the fuel cell at 1000°C degree. In one experiment using carbon powder as fuel, the carbon was pre-charged into the cell and then heated up to 1000°C degree. No more carbon was added during 20 hours course of testing.

A modified liquid anode fuel cell was also made and tested as shown in Fig 4 at right. In this configuration the molten anode was outside the electrolyte tube and was encased by a supporting structure. Cathode was inside an electrolyte tube and Pt gauzes and wires were used as cathode current collector. Plastics of PE, PP and PS, wooden pellets and diesel were manually dropped into the fuel cell. This modified (reverse) cell had more space in its anode chamber than a standard cell.

Commercial virgin plastic pellets were used and they weighed from 17 to 27 mg each. When these were dropped into the cell, it took about 3 seconds for gaseous fumes (smoke) to come out of the cell. The release of fumes by each pellet was brief though, only lasted about 7 to 10 seconds. The gaseous fumes were collected and analyzed by Agilent M200H MicroGC. Its power output was measured by Chroma DC Electric Load. When the cell was fully charged and no electric load was applied, plastic was only subjected to pyrolysis and its gaseous fumes were not oxygenated. When an electric current was drawn, its gaseous exhaust became oxygenated. The liquid anode cell produced electricity both during plastic addition and when the addition ceased. At fuel cell mode each new plastic pellet was added when its OCV dropped to 0.80 volt. Its fuel efficiency was calculated by using the total power output produced during gasification (plastic addition) and residual carbon (when the addition ceased).

**RESULTS AND DISCUSSION**

Dropping of plastics into a hot liquid anode resulted in immediate pyrolysis, forming gaseous fumes, soots and residuals (carbon). In one experiment, pyrolysis of polyethylene, polypropylene and polystyrene at 1000°C yielded significant amounts of...
residual solid masses, being 19 wt%, 28 wt% and 64 wt% respectively. In the gaseous fumes hydrogen was found to be the main component (70-80%) and CH₄ was the second (20-30%). Trace or small amounts of ethane, ethylene, acetylene, propane, CO and CO₂ were found also, but their concentration was much smaller, less than 1 percent.

Fig. 5 shows power outputs of a standard liquid anode cell with a pre-charged carbon. The cell ran continuously for 20 hours with a single charge of carbon (10 grams) at fuel efficiency of 48%. Earlier results had indicated a higher fuel efficiency of 62% in a different set-up.

The direct carbon conversion in a liquid anode at 1000°C can be summarized as:

\[ C + O₂(g) = CO₂(g) \quad \Delta G = -94.6 \text{ kcal/mol} \quad [10] \]
\[ 2C + O₂(g) = CO(g) \quad \Delta G = -107.1 \text{ kcal/mol} \quad [11] \]
\[ 2\text{CO}(g) + O₂(g) = 2\text{CO}_2(g) \quad \Delta G = -82.1 \text{ kcal/mol} \quad [12] \]

and their corresponding electrochemical reactions are:

\[ C + 2\text{O}^- = \text{CO}_2(g) + 4e^- \quad \text{OCV} = 1.03 \text{ volt} \quad [13] \]
\[ C + \text{O}^- = \text{CO}(g) + 2e^- \quad \text{OCV} = 1.16 \text{ volt} \quad [14] \]
\[ \text{CO}(g) + \text{O}^- = \text{CO}_2(g) + 2e^- \quad \text{OCV} = 0.89 \text{ volt} \quad [15] \]

Fuel efficiency of a direct carbon conversion is believed to be inherently higher than hydrogen solid oxide fuel cell as some predicted as high as 80% [John Cooper (7)]. In a liquid anode the maximum efficiency was estimated to be close to 70% without any co-gen. One interesting feature of direct carbon conversion is that there may exist a minimum fuel efficiency of 39.1% assuming no ohmic and polarization losses. Unlike hydrogen in a fuel cell where it can be carried out by exhaustive steam, solid carbon has to be gasified first: the minimum efficiency to convert to CO is 39.1%.

Carbon gasification reaction by CO₂ has been suggested also in a liquid anode,

\[ C + \text{CO}_2(g) = 2\text{CO}(g) \quad \Delta H = 40 \text{ kcal/mol} \quad \Delta G = -12 \text{ kcal/mol} \quad [16] \]

this reaction is strongly endothermic and at temperatures above 700°C it becomes spontaneous. Because this process occurs in situ at liquid anode, it should not cause any parasitic loss of fuel efficiency.

Actual power outputs of a standard liquid anode cell with polypropylene as fuel is shown in Fig 6. Even after plastic addition was ceased, the cell continued to produce electricity but at a slower rate. Fig 7 shows fuel efficiencies of direct plastic conversion in a standard liquid anode cell at various power outputs. Polystyrene had a higher fuel efficiency (43%) than polyethylene (25%) and polypropylene (30%) because its pyrolysis produced more soot/residuals and less gaseous fume. However in a modified liquid anode cell (shown in Fig 4 right) with a larger anode chamber all plastics yielded higher fuel efficiency.
efficiencies (45-48%) as shown in Fig 8. Fuel efficiency for wood pellets (Eureka Premium, Missoula, MT, USA) was estimated based on heating value from supplier.

CONCLUSIONS

Carbonaceous matters including diesel, plastics and biomass thermally decompose when subject to temperatures higher than 600°C. The ultimate decomposition products are small gaseous molecules such as hydrogen and solid carbon. Liquid anode fuel cell has demonstrated its ability to directly convert carbonaceous matters including plastics to electricity with fuel efficiency greater than 48%.

ACKNOWLEDGEMENTS

Direct waste plastic to energy conversion is supported by DARPA under contract #W911QY-04-2-003. The author would like to thank DARPA and Rosemarie Szostak, Don Pickard and Leigh Knowlton for their support. The author would like also to express thanks to current and former scientists, engineers and technicians of CellTech Power, Inc. engaged in liquid anode R&D from 1997 to present, Bai Wei, Adam Blake, Jack Shindle, Scott Rackey, Steve Andrews, Linda Bateman, Gary Bingle, Oren Bernstein, Reinder Boersma, Frank Brewer, Glenn Duchene, Andrew Gustafson, Ed Kelrikh, Jason Kwa, Ken Manwiller, Scott Mastroianni, Frank Qi, Mike Slaney, Gouhou Wang, Zena Uzep, Gail Graveson, Jason Boyer, David Hammer, Robyn Bonin, Alex Lehman, Cheryl Gendron and William Acton.

REFERENCES

1. A. B. Hart and G. J. Womack, Fuel Cells, Theory and Application, p. 3-7, Chapman and Hall Ltd, London.
2. US Patent 460,122, September 29,1891.
3. H. Arthur Klein, Fuel Cells, An Introduction to Electrochemistry, p. 120-124, L. B. Lippincott Company, Philadelphia & New York.
4. GB Patent 126,766, June 16, 1919.
5. US Patents 3,741,809, June 26, 1973 and 3,970,474, July 20, 1976.
6. US Patent 6,200,696 B1, March 13, 2001.
7. J. Cooper, et al., Turning Carbon Directly into Electricity, pp. 4-12, S&TR, June 2001; Direct Carbon Conversion: Application to the efficient conversion of fossil fuels to electricity, Fall Meeting of the Electrochemical Society, Paper No. 50, Phoenix AZ, October 2000; DOE Direct Carbon Fuel Cell Workshop, NETL, Pittsburgh, PA, July 30, 2003.
8. US Patent 6,692,861, February 17, 2004.
9. T. M. Gur and R. A. Huggins, J. Electrochem. Soc., 139 (10), L95-L97 (1992).
10. GB Patent 940,900, November 6, 1963; US Patent 3,432,352, March 11, 1969; US Patent 3,138,490, June 23, 1964.

11. C. Bruno, European Patent Application 333,261, September 20, 1989.

12. I. Yentekakis, et al., Ind. Eng. Chem. Res., 28 (9), 1414-1424 (1989).

13. T. Horita, N. Sakai, H. Yokokawa, T. Kawada and M. Dokiya, UK patent application GB 2278010, published 11/16/1994.

14. T. Tao, et al., US Patent Application No. 09/837,864 and PCT/US02/37290.

15. T. Tao, et al., US Patent application No. 10/300,687, PCT/US02/37290, PCT/US02/020099, US Patent Application No. 60/391,626, US Patent Application No. 60/354,715 and PCT/US03/03642, US Patent Application No. 60/492,924, US Patent Application No. 09/837,864 and PCT/US02/37290, ZA Patent No. 2002/86111.

Figure 1. A two-cell direct carbon conversion liquid anode stack.

Figure 2. Liquid anode fuel cell stack and system. At left a 30-cell stack; at right a kilowatt liquid anode system using hydrogen and natural gas.
Figure 3. OCV of reaction $M + O^{2-} \rightarrow MO_2 + 2e^-$ as a function of temperature.

Figure 4. Liquid anode fuel cells. At left a standard configuration. At right a modified configuration with liquid anode outside electrolyte tube.

Figure 5. A standard liquid anode cell with pre-charged carbon powder (10 grams).
Figure 6. Power outputs in a standard liquid anode cell (anode inside) with PP as fuel.

Figure 7. Fuel efficiency of direct plastic conversion in a standard liquid anode cell.

Figure 8. Fuel efficiency of direct fuel conversion in a modified liquid anode fuel cell with wood pellets, diesel, PE, PP and PS.