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CONSIDERATIONS OF THE CONVERSION TECHNOLOGY FOR BIOMASS AS AN ENERGY SOURCE

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Summary

Various aspects of the technology for using biomass as an energy source are considered. Estimates of the amount of product energy recoverable from a given conversion process are made. Direct combustion, gasification, pyrolysis, catalytic liquefaction and fermentation are considered. Direct combustion is the most efficient use of biomass as a fuel. The other technologies, with the exception of gasification, are far behind in efficiency and state of development.

INTRODUCTION

Increasing energy demands on a world wide scale have not been met by increases in the availability of petroleum and natural gas. This availability crisis has resulted in ever rising costs of traditional fossil fuels which has stimulated interest in identifying alternative energy sources. Many factors indicate that the use of solar energy stored by plant photosynthesis should be considered. Biomass, living matter, represents a large, renewable resource that can be used as feedstocks for energy producing processes.

NATURE AND AVAILABILITY OF BIOMASS

Biomass is defined as organic matter such as trees, plants, agricultural crops, and grasses which can be grown specially as feedstocks for energy producing processes. Biomass uses sunlight energy to photosynthetically convert carbon dioxide and water into carbohydrates and oxygen. The carbohydrates contain more stored chemical energy than CO₂ and H₂O. This photosynthetic energy conversion has an overall efficiency of 0.1% to 1% of the total available sunlight in temperate zones.¹

Biomass, as defined above, includes forestry and agricultural residues but excludes sewage sludge, animal manures and aquatic crops. Municipal solid waste is also excluded, but many energy production processes developed for MSW feedstocks have been applied to biomass. Although agricultural and forestry residues have undesirable processing characteristics, i.e. high moisture contents, they are abundant, available over a wide geographic area and have little or no economic value. They can serve as trial or demonstration feedstocks before large scale energy farms are feasible.

Many feedstock inventory studies have been completed^{2,3,4,5} in addition to the standard, annual surveys conducted by the U.S. Department of Agriculture and the U.S. Forest Service. The quantities of energy feedstocks available as residues produced by existing forestry and agricultural techniques are summarized in Table 1. MSW quantities are included for comparison.

The variation in amounts reported in Table 1 can be attributed to the definition of 'residue' and 'available'. An agricultural residue is any material remaining after the desired portions of the plant have been removed. Forestry residues include those portions

Table 1. Biomass Resource Availability

Biomass Type	10 ⁶ Oven Dry Tons Available	Ref.
Agricultural Residues	418.7	5
	278	3
	400	6
	337	7
Forestry Residues	65.102	7
	67.9	4
	80	6
	128	8
	125	9
MW	115	10
	105	6
	100	9

of the tree that accumulate during logging and wood manufacturing processes. "Available" indicates that the competing use for the resource is of less value than energy production, or that the residue is not being used at present. These definitions are often not adhered to in reporting residue amounts. It must also be noted that the quantities are in terms of dry tons of organic matter which accounts for the low values for MSW.

Another measure of the amounts of a biomass resource is its energy equivalency. This is obtained by multiplying the amount of biomass by its energy content (higher heating value in BTU/lb). For instance, in energy terms, there are 1.2 quads of energy per year available from forestry residues and 6.1 quads from agricultural residues.⁵ In addition, the Department of Energy reports¹¹ that out of a proven domestic reserve of 300 quads in standing forests, annual growth produces an additional 7 to 8 quads (proven domestic reserves of oil are 200 quads; gas are 300 quads). Already 4 quads of forest biomass are used annually for lumber and paper products. These operations generate the 1.2 quads mentioned above. Thus, 3-4 quads of energy could potentially be generated from forest biomass each year, without touching the standing forests. Salo and Henry¹⁰ put this amount at 7 quads per year.

The value of a specific crop, agricultural or forestry residue depends on its availability, abundance, and energy content. Availability on a geographical and seasonal basis is an important factor influencing the use of agricultural residues, but seasonality is unimportant for forest biomass. Average values for the energy content and composition of many crops and forest species are given in Table 2, (see also ref. 1, 4,5,8).

Table 2. Nature of Biomass

Biomass	N ₂ [*]	S [*]	H ₂ O [*]	Ash [*]	Energy Content [†] Btu/lb
'Trees'	<1.5	<0.1	45-55	<2.5	7800-9600
'Agriculture'	0.4-4.5	<0.2	>55	4-20	7500-8000

* Wt. percent

† higher heating value of dry biomass

CONVERSION OF BIOMASS TO ENERGY

Biomass as a feedstock imposes a number of a priori constraints on the conversion process for obtaining energy or fuel. Biomass as received at the plant 'gates' has a very high moisture content - about 50% as compared to MSW which contains about 25%. It is a difficult solid to handle because of the variety of sizes, shapes and textures. Biomass undergoes physical and chemical changes during storage, a characteristic made more troublesome by the seasonal availability of some biomass. Biomass by its diffuse nature also dictates small conversion plant sizes compared to that normally encountered in the electrical utility and chemical processing industries. Conversion units should be economical in the sizes of 1000 dry tons to 2000 dry tons of biomass feedstock per day. The feedstock with the greatest potential for energy generation is forestry residues. Crop residues, although produced in larger amounts were deemed unsuitable because of their greater moisture content, lower area concentration and the adverse ecological effects of their removal from the fields.⁴

There are two fundamental methods of converting biomass to energy: thermochemical conversion and biochemical conversion. The process types which are best suited for conversion of wood to energy/fuel are listed in Table 3.

Table 3. Biomass-to-Energy Conversion Processes

Thermochemical Conversion		Biochemical Conversion
Direct Combustion	Pyrolysis	Fermentation
Gasification	Liquefaction	

Emphasis will be placed on direct combustion of biomass in boiler plants and conversion of biomass to liquid and gaseous fuels for use in combustion turbines. The nature and current state of development of each of these processes is summarized below.

Direct Combustion

Direct combustion of wood and recovery of the heat of combustion is the simplest and most extensively used energy conversion process for biomass. Combustion is the chemical combination of oxygen with the carbon and hydrogen in wood to yield CO₂, H₂O and heat. The value of wood as a fuel depends on its heat content, moisture content, ultimate and proximate analyses. The higher heating value is obtained by combustion of dried wood in a bomb calorimeter. The products are CO₂ and liquid water. HHV is about 8000 Btu/lb for softwoods and around 9000 Btu/lb for hardwoods. Extensive tabulations of heats of combustion for forest species are given by Tillman⁸, Shafizadeh¹², de Groot¹³, Karchesy and Koch², and boiler manufacturers¹⁴.

The available heating value (HHV x wt.% wood) of the wood depends on the moisture content. The first step in the combustion of wood is vaporization of water, followed by vaporization, then combustion of volatile organics and lastly the burning of the fixed carbon. The proximate analysis gives the relative amounts of moisture, volatiles and fixed carbon in the fuel. The amount of air, the usual source of oxygen, required for complete combustion can be calculated from

Table 4. Representative Analyses of Fuels

	Hardwood ¹		Softwood ⁶		Coal ⁶		Residual ¹
	Wood	Bark	Wood	Bark	Utah	Pittsburgh	Fuel Oil
Proximate Analysis %							
Moisture	--	--	--	--	5.0	3.0	
Volatiles	77.3	76.7	81.5	73.0	47.6	33.9	<.1
Fixed Carbon	19.4	18.6	17.5	26.0	48.3	55.8	
Ash	3.4	4.6	1.0	1.3	4.1	10.3	
Ultimate Analysis %							
C	50.8	51.2	52.3	56.2	77.9	75.5	86.5-12.0
H	6.4	6.0	6.3	5.9	6.0	5.0	9.5-12.0
O	41.8	37.9	40.5	36.7	9.9	4.9	--
N	0.4	0.4	0.1	0.0	1.5	1.2	--
S	0.0	0.0	0.0	trace	0.6	1.3	.7-3.5
Ash	0.9	5.2	0.8	1.2	4.1	10.3	0.01-.50
Btu/lb dry	7827	7593	9,050	9500	14,170	13,650	17,410-18,990

the ultimate analysis or chemical composition of the fuel. Excess air from 25% to 40% is used to ensure complete combustion.¹⁵ Representative proximate and ultimate analyses of wood are given in Table 4. Data is also given for fossil fuels. Note that wood is much higher in moisture content, and oxygen, but lower in sulfur and ash.

Before wood can be used as a boiler fuel, it is usually processed to reduce its size, to remove moisture and perhaps to increase its density. Large pieces of wood are usually put thru an attrition mill or 'hog' for size reduction. Moisture is removed by mechanical pressing, air drying, or rotary drum dryers using direct contact of hot gases. Drying hogged fuel results in higher boiler efficiencies and lower emission. Densification of wood can give a fuel product of uniform size, and shape with a density about 5 times greater than that of the feed wood. However, densification requires about 7 to 12% of the energy in the product in addition to increased capital and operating costs. Details of densification processes can be found in a recent report by Reed and Bryant.¹⁷ Karchesky and Koch¹ have reviewed all wood fuel preparation systems.

Once the wood has been prepared for burning, it is fed to specially designed boilers. There are basically two classes of wood burning furnaces: grate or spreader-stoker burners and suspension burners. Grate and spreader-stoker burners burn the biomass on a grate in a pile or thin layer. They can handle large wood residues in the form of hogged fuel with moisture contents as high as 55%.¹⁸ In suspension burning systems, the wood is supported by air during combustion. They require very fine, pulverized wood particles (sawdust) which contain less than 15 wt% moisture. Details of these boilers are given by Bliss and Blake,¹⁹ and Pingrey.¹⁸

Wood fired boilers for steam generation have efficiencies ranging 60% to 80%.¹⁴ Pingrey²⁰ reports average steam boiler efficiencies of 62-69% based on a survey of users in the pulp and paper, forest products and utility industries. Increased moisture content decreases boiler efficiency since energy is lost in vaporizing the water and raising it to the temperature of the stack gases.¹ The overall conversion efficiency for conventional steam generation of electricity from wood is around 25%. Details are summarized in Table 5.

Assuming an overall conversion efficiency of 25% for conventional steam generation of electricity from wood the amount of wood necessary for a certain generating capacity is given in Table 6.¹

Table 6. Wood* Required for Electrical Generation

Generation Size	Green Hardwood as Fuel
5 MW	7.5 ton/hr
25 MW	37.5 ton/hr
250 MW	375 ton/hr
500 MW	750 ton/hr

* 42% moisture content

Estimates by Pingrey²⁰ indicate that there are about 4500 MW of generating capacity that use wood as a fuel. 3600 MW is produced by the Pulp and Paper Industry, 800 MW by the Wood Products Industry, and 60 MW by utilities in Eugene, Oregon, Libby, Montana, Ashland, Wisconsin and Burrington, Vermont. In January 1978, Pacific Gas and Electric reports²³, purchasing 15.2 MW in 1977 from wood-fueled generators, and is considering total projects totaling 71-95MW of co-generating capacity fueled by wood waste. Proposals for 7 wood fired projects with generating capacities ranging from 1 to 25 MW are being considered by NRECA.²⁴ Utilization of wood as a fuel for electrical generation is increasing. Decisions concerning its suitability as a fuel are being continually reevaluated in terms of availability and cost, not in terms of technology.

Gasification

Gasification is the thermal decomposition of biomass in the presence of limited amounts of air/oxygen. First drying of the wood, then vaporization of the volatile organic components occurs, followed by some thermal cracking, but little oxidation of these gases. The remaining carbon char will be partially oxidized in the presence of oxygen, carbon dioxide and steam. The reactions are summarized by Radovich, et al.⁵ and SERI²⁵. Depending on the operating conditions (temperature and pressure) and the amount of steam added, the relative amounts of CO, CO₂, H₂, CH₄, and light hydrocarbon gases in the product fuel can be varied. Steam is usually injected to maximize the amount of CO and H₂ produced by reacting with the carbon char. Operating temperatures range from 2200-3000°F for gasifiers operating near atmospheric pressure. Higher pressure operation can give greater amounts of CH₄ in the product gas. The product gas has a heating value of 150-350 Btu/SCF depending on whether air or oxygen is used for gasification. Research on the use of catalysts is also being studied²⁶ because catalysts give higher quality gas yields at less severe operating conditions. The operating conditions, typical gas yields and compositions

Table 5. Efficiency for Wood to Electricity Conversion

Efficiency %	Heat Rate Btu/kwh	Generation Size MW	Wood Moisture %	Ref.
25	13,648	--	42	21
21.3	16,018	49.6	50	22
20.9	16,300	20	--	22
22.4	15,200	40	--	22
31.1	10,950	55	50	19

Table 7. Gasification Process Details

	Operating Conditions		Product Composition: Vol. %		
	Purox	Moore-Canada	Purox	Moore-Canada	
T, °F	3000	2200	CO	35.7	25.0
Press., psig	0	3-6	H ₂	28.9	20.0
reactants	O ₂	air-steam	CO ₂	23.4	9.3
product yields (SCF/dry ton)	20,000	40,000	CH ₄	10.1	3.7
			N ₂	1.7	41.5
Btu/SCF	280-350	180	O ₂	--	0.5

for an oxygen blown gasifier (Purox) and an air blown gasifier (Moore-Canada) are given in Table 7 for a wood waste feedstock.⁵

The energy conversion efficiency, HHV of biomass feed is 81.1% for the oxygen gasifier and 78.8% for the air-blown gasifier based on oven dry biomass fuel. Detailed material and energy balances plus efficiency calculations can be found in the report by Radovich, et al.⁵ The recent SERI survey of all aspects of biomass gasification should also be consulted.²⁵

Although biomass gasifiers are in the demonstration stage of development, (60-200 dry tons per day) the product gas potentially has many uses. This is illustrated in Figure 1.

Combustion

Combustion of the product gas from the gasifier systems currently under development is attractive if the furnace is on-site. This gas cannot be stored effectively and very large volumes would have to be transported (at high cost) to supply energy equivalent to natural gas. Furnaces equipped with burners specifically designed for low BTU gas, can give efficiencies of about 80%. Combustion considerations for this fuel gas can be summarized as follows:²⁷

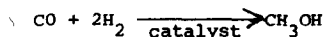
"A low BTU gas roughly requires an equivalent volume of air to complete combustion, whereas natural gas requires 10 times the volume of air over the volume of gas to be burned. The result for the same heat release, is that low BTU gas streams create products of combustion that are 30 to 40 percent greater in volume than that from natural gas."

Gas Clean-Up

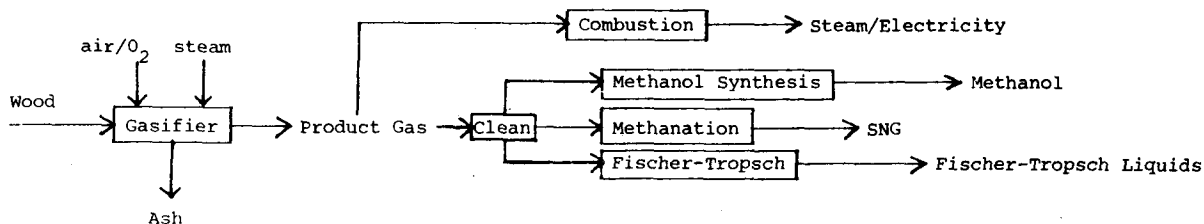
The raw product gas must be 'cleaned' before it becomes a suitable synthesis gas (H₂ + CO) for SNG, methanol or Fischer-Tropsch liquids. Acid gases, H₂S and CO₂ are removed by absorption and reaction in suitable liquids^{22,28,29}. If necessary, cryogenic separation of light hydrocarbon gases is also done. Finally, the required H₂/CO ratio in the synthesis gas is accomplished by the water-gas shift reaction (H₂O + CO → H₂ + CO₂) over suitable catalysts. About 88.7% of the raw product gas is available as synthesis gas.²⁹

Methanol Synthesis

The basic synthesis reaction for methanol synthesis is

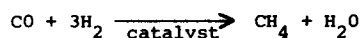


The technology for synthesis of methanol from synthesis gas dates from the mid-1920's. Process development in this area has continued, with about six companies offering conversion schemes with operating conditions ranging from 40-300 atm and temperatures of 221.1-282.2°C (430-540°F). Reactor design, heat recovery, and recycle flows vary from process to process. Feedstock requirements are a 2/1 ratio of H₂/Cp (stoichiometric amount), small amounts of CO₂ (<0.2%) and about 1.1% inerts (N₂, etc.). All sulfur compounds must be removed from the feed because methanol catalysts are very sensitive to their presence. Conversion of H₂ + CO is as high as 97% for the Chem Systems low pressure process²⁹. In that process, 81.5% of the heating value of the feed synthesis gas is recovered in the methanol product. Thus, about 58% of the feed energy would be recovered in the HHV of the methanol product.



Methanation

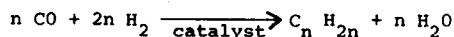
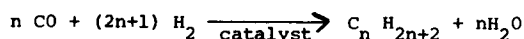
Production of methane can occur by the reaction



Methane produced in this manner is commonly referred to as substitute natural gas (SNG) because natural gas is about 85% CH_4 . The Metric Report¹⁹ reviews the existing process approaches for methanation. About 95% of the synthesis gas is converted to SNG. This means that 84% of the heating value of a raw product gas (280 BTU/SCF) is recovered in the SNG. SRI²² reports that about 63% of the wood feed's HHV would be recovered in SNG.

Fischer-Tropsch Synthesis

An alternative route to liquid fuels after gasification is Fischer-Tropsch Synthesis which is represented by the reactions:



The feed gas for this process should have a 1.7-2.8 ratio of H_2 to CO, and low inerts (<1.1%).

There are two operating schemes for Fischer-Tropsch Synthesis. Fixed bed operation at 232.2°C (450°F), 370 psig requires a H_2/CO feed ratio of 1.7 and converts 65% of the $\text{H}_2 + \text{CO}$. About 41% of the heating value of the raw feed gas is recovered as liquid products. The fluid-bed operates at 329.4°C (625°F), 320 psig. The H_2/CO feed ratio is 2.8 and conversion is 85%, but this process gives lower yields of high molecular weight hydrocarbons. About 60% of the heating value of the feed gas is recovered as liquid products (C_3^+). Excess (> plant requirements) fuel gas is also produced. Therefore, about 48% of the higher heating value of a wood feed would be recovered in the hydrocarbon liquids.⁵

Pyrolysis

Pyrolysis is the thermal decomposition of carbonaceous materials by indirect heat transfer in the absence of O_2 , without addition of steam or carbon monoxide to the reactor. Pyrolysis is similar to the old wood distillation process. Operating conditions are 900-1700°F, and atmospheric pressure. Pyrolysis produces varying amount of liquids, gases, and chars depending on the nature of the feedstock. The liquid products contain highly oxygenated organics (organic acids) which are partially soluble in water and thus corrosive. Liquid product yields are maximized by rapid heating rates (short residence times) to moderate temperatures (1000°F) and immediate quenching of the gases and condensable vapors. This prevents cracking of the organic liquids. Product gases consist mainly of CO, H_2 , CO_2 and CH_4 . Approximately 45-60% of the feed mass (dry basis) shows up in the liquid and gaseous products. Non-condensable gas yields are maximized by holding the char and volatile components at high temperatures for long residence times. The remaining carbon will be in the residual char, which also may contain up to about 40% of the original heat content of the feed.

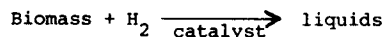
The pyrolytic oil is slightly corrosive to mild steel due to its carboxylic acid and H_2S content,

requiring the use of stainless steel piping and storage. It is hydrosopic and must be handled appropriately to prevent increases in water content; 14% water is normally maintained to reduce the viscosity. The oil has a lower heating value than No. 6 fuel oil and must be atomized at a higher temperature; it will be necessary to provide separate burner jets. All of the above, require special handling requirements such as separate storage, piping, and burner facilities. The ash content is less than 1.0%, allowing use in facilities without ash handling equipment. Also, pyrolytic oil has a lower sulfur content than No. 6 fuel oil. It could be used in large industrial applications that are using No. 6 fuel oil to meet emission standards.

Typically, a rapid, moving bed flash pyrolysis system yields 44% of the BTU content of the feed in the oil product. The gas and char are used internally. A fixed bed pyrolysis unit such as the Tech-Air system⁵ will give 50% of the HHV of the feed in the product char and oil. The oil only contains 13% of the feed HHV.

Catalytic Liquefaction

If biomass is to be liquefied, hydrogen must be added at high temperatures and pressures. Appreciable amounts of hydrogenation can occur, according to the following catalyst-promoted reaction:

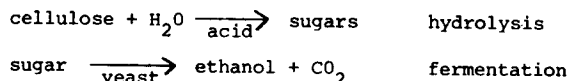


One such process is the carboxylolysis process being developed by DOE. Carboxylolysis is the catalytic conversion of cellulose to oil in the presence of carbon monoxide and water. The biomass is hydrogenated at 600-700°F and 2000-4000 psi in the presence of the sodium carbonate catalyst. This process is being tested at a 1 dry ton/day pilot plant in Albany, Oregon.

The oil product is very viscous and corrosive. It would require special burners and handling facilities. About 58% of the energy content of the wood is recovered in the oil.⁵

Fermentation

Ethanol can be produced from cellulosic material by a combination of hydrolysis and fermentation. The hydrolysis and fermentation steps are:



Wood contains 90-95% cellulose, hemicellulose and lignin. Pretreatment of the wood to obtain the fermentable sugars can be accomplished with acids such as sulfuric and hydrochloric or with hydrolytic enzymes (MITRE). The conversion of sugar to ethanol by yeast cells includes such steps as sterilization, microorganism preparation, pasteurization, fermentation, centrifugation and distillation. About 24.5% of the energy content of the wood is obtained in the ethanol.

COMPARISON OF CONVERSION PROCESSES

Table 8 summarizes the output/input efficiency for each biomass-to-energy conversion process. This ratio is not a measure of overall system efficiency because none of the energy losses nor the parasitic energy requirements of each process step have been considered. It only indicates the relative amount of energy (HHV) in the product compared to the HHV of the woodfeed.

Table 8. Ratio of Energy Out/Energy In
For Biomass Conversion Technology

Energy Product	Conversion Method	Efficiency: Btu Out/Btu In
Electricity	D.C.	21.3 - 31.1
Steam	D.C.	60 - 76
SNG	G,M	63
Methanol	G,MS	57
F.T. Liquids	G,FTS	48
Ethanol	F	24.5
Low/Med. Btu Gas	G	80
Pyrolytic Oil	FP	44
Pyrolytic Oil & Char	P	50
Liquefaction Oil	CL	58

Legend: D.C. = direct combustion
G = gasification
M = methanation
MS = methanol synthesis
F.T.S. = Fischer-Tropsch synthesis
P = pyrolysis
FP = flash pyrolysis
CL = catalytic liquefaction

Overall system efficiencies inferred from this data should be used with caution because the overall efficiency is a function of the individual component efficiencies and how they are assembled in the final process scheme.

A final comparison is made in Table 9 which lists the efficiency for producing steam from the various energy products.

Table 9. Steam Conversion Efficiency
for Wood Derived Fuels

Fuel	% Steam Conversion Efficiency
Wood	60-76
Low/Med BTU Gas	60.8
SNG	47.9
Methanol	45.6
Ethanol	19.6-37.5
Liquefaction Oil	43.5
Pyrolytic Oil & Char	37.5
Pyrolytic Oil	33
Fischer-Tropsch Liquids	38.4

A furnace efficiency of 76% for the gases and 80% for methanol and ethanol, but only 75% for the poor quality pyrolytic and liquefaction oils was assumed.

CONCLUSIONS

Direct combustion is presently the most efficient way of utilizing wood as a source of energy. Direct combustion is a well developed, commercial technology

Gasification is at the demonstration - near commercial stage, but the other conversion processes for wood are at the bench scale or pilot plant level.

The above analysis neglected many important factors which will greatly influence any use of biomass as an energy source. Feedstock collection, cost and long term availability; conversion costs, environmental impacts (such as increased particulate emissions with combustion or loss of soil nutrients due to residue removal) must all be considered.

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DEVELOPMENT OF SULFUR-TOLERANT COMPONENTS FOR THE MOLTEN CARBONATE FUEL CELL

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ABSTRACT - The sulfur tolerance of candidate anode and anode current collector materials for the molten carbonate fuel cell were evaluated in an electrochemical half-cell using both steady-state and transient potentiostatic techniques. H_2S was introduced into the fuel at concentrations of 50 and 1000 ppm. At the higher sulfur concentration using low-Btu fuel, both nickel and cobalt were observed to undergo a negative shift in their open-circuit potentials, and high anodic and cathodic currents were observed compared with clean fuels. Kinetic currents measured using the transient potentiostatic technique were not greatly affected by 50 ppm H_2S introduced into the fuel. However at higher sulfur concentrations, higher kinetic currents were observed, indicating a probable sulfidation reaction. Of the new anode materials evaluated $Mg_{0.05}La_{0.95}CrO_3$ and TiC showed good stability in the anodic region. With the former material, exchange current densities in low-Btu fuel were calculated to be $\approx 11 \text{ mA/cm}^2$ at 650°C , lower values than found for either nickel or cobalt anodes under similar conditions.

Of the anode current collector materials evaluated, high stabilities were found for 410 and 310 stainless steels. The implications and relevance of these results on fuel cell performance is discussed here.

INTRODUCTION

The essential components which comprise the molten carbonate fuel cell are a porous anode and a porous nickel oxide cathode, which are separated by an ionically conducting molten carbonate mixture supported on a lithium aluminate matrix, both components together being commonly referred to as the tile. To date, these fuel cell components have shown good electrochemical performance and corrosion stability under cell operating conditions over several thousand hours in the absence of sulfur-containing species in the fuel and oxidant. However, commercialization of this system for electric utility power plants will dictate that the fuel cell will operate on fuel oils in the short term and on the products of coal gasification in the longer term, all of which can be expected to contain sulfur. Two general approaches can be followed towards solution of the sulfur problem in the molten carbonate fuel cell: The first approach is to completely remove the sulfur contaminants from the fuel cell before entry into the fuel cell anode. The second approach is to determine the sulfur tolerance of currently used cell components. Then, when degradation in cell performance and materials stability becomes evident, the next step is to identify, characterize, and develop sulfur-tolerant components that show acceptable long-term electrochemical performance under defined sulfur concentrations within the overall system. It is the second of these two approaches which will be discussed here. Previous literature (1) has indicated that the catalytic activity of nickel may be poisoned because of the H_2S chemisorption at the temperatures present in the molten carbonate fuel cell ($\approx 650^\circ\text{C}$), which may result in the formation of nickel sulfide (1) at the porous nickel anode, possibly resulting in a loss of structural integrity and electrocatalytic activity (2,3).

No work has been reported on the corrosion of nickel by sulfide or sulfate while in the presence of molten carbonate fuel cell. Most work reported to date has focused on nickel in contact with various sulfur-

containing gases. For example, the corrosion rate of nickel either in pure SO_2 or in SO_2/O_2 mixtures has shown parabolic gravimetric kinetics, which can result in the growth of external NiO and internal Ni_3S_2 scales and at temperatures above 645°C the Ni_3S_2 in contact with nickel becoming liquid. There has been some evidence for the growth of an inner Ni_3S_2 layer within nickel (4) via diffusion of SO_2 through open channels or crevices in the initial oxide layer. The overall rate of this process is probably diffusion of nickel through the Ni_3S_2 phase in the nickel oxide matrix.

Large-scale molten carbonate fuel cells will require the implementation of a catalytic burner between the anode outlet and the cathode inlet for CO_2 management for the maintenance of the desired electrochemical process. This requirement will introduce sulfur to the cathode originating from the anode inlet which, under the oxidizing conditions present there, will occur as SO_2 and can be expected to readily absorb into the molten carbonate mixture present both at the porous nickel oxide cathode and within the tile by the equilibrium reaction: $M_2CO_3 + SO_2 + 1/2 O_2 \rightarrow M_2SO_4 + CO_2$ which can be expected to strongly favor the formation of the alkali metal sulfate. The concentration of sulfur species at the anode may possibly be influenced by electrochemical transport of sulfur species (initially present as sulfate) from the sulfur-contaminated cathode and may well have an impact of the long-term stability of the anode.

The emphasis of the work reported here is on electrochemical halfcell measurements on presently used anode and anode current collector materials with both clean and sulfur-containing fuels. By this means, the effect of such sulfur-containing species on their chemical stability and electrode kinetics can be evaluated. The initial selection of candidate sulfur-tolerant components for the molten carbonate fuel cell included materials which had previously shown evidence of extended stability when used in applications such as methanation catalysis, positive electrode current collector components of high-temperature metal/sulfur batteries and interconnect materials used in solid-oxide fuel cells. The latter materials, which included $Mg_{0.05}La_{0.95}CrO_3$, were of particular interest because they had shown previous high stability to both oxidizing and reducing conditions in the high-temperature solid oxide fuel cell. These materials were initially subjected to preliminary corrosion testing by simulating those chemical conditions expected in the anode environment of the system. Materials evaluated as sulfur-tolerant anodes in the electrochemical half-cell have included nickel, cobalt, CoMo, CoW, WC, TiC, $Mg_{0.05}La_{0.95}CrO_3$, Cr_2O_3 (doped with TiO_2), and NbN. Materials for the anode current collector have included hastelloys, kanthal, 400 and 300 stainless steels, and iron aluminum manganese and iron aluminum molybdenum alloys. The relative stabilities of these materials at the anode and anode current collectors for the molten carbonate fuel cell and a comparison of the electrocatalytic behavior of the candidate anodes selected will be discussed.

EXPERIMENTAL

The initial corrosion screening of selected candidates was performed by partially immersing in a lithium/potassium carbonate mixture at 650°C contained in ceramic boats within an alumina tube, through which was equilibrated on different occasions both clean and

sulfur-containing fuel gas.

Materials for the anode and anode current collectors were obtained from commercial sources (Materials Research Corporation, Orangeburg, New York and CERAC, Inc., Milwaukee, Wisconsin). All electrochemical measurements were performed in a half-cell system. The working electrodes were attached to an alumina-sheathed current collector fabricated from 316 stainless steel wire. For nickel and cobalt, however, the current collectors were made from nickel and cobalt, respectively. A gold wire bubbled with 33.3% O_2 -66.7% CO_2 inside an alumina tube served as a reference electrode. The gold was in contact with the melt via a small hole (0.015-inch diameter) at the bottom of the tube. All measurements were performed in electrolyte of composition 62 mole percent Li_2CO_3 -38 mole percent K_2CO_3 at 650°C. The counter electrode used in this work consisted of Palau of nominal composition 80% Au, 20% Pd, which proved to have a higher sulfur tolerance than a pure gold counter electrode, the usual material used by us when clean fuels are used in electrochemical half-cell work. Fuels with a predetermined high-sulfur content or pure H_2S were mixed into the primary fuel after the humidification step at the rate required to achieve the desired sulfur content. Experimental observations in this work indicated some apparent sensitivity of the open-circuit potential obtained at both nickel and cobalt electrodes to the presence of H_2S introduced into the fuel gas. At concentrations of 50 ppm and below, such variations in the open-circuit potential were found to be somewhat erratic and were not completely reproducible. Apart from some variations in the open-circuit potential, steady-state polarization curves for clean fuel and fuel containing 50 ppm H_2S were of almost identical slope, indicating little evidence of electrode poisoning. Polarization data were performed in both low- and high-Btu fuels corresponding to the respective compositions 21.4% H_2 , 17.7% CO , 9.2% CO_2 , 1.1% CH_4 , 45% N_2 , 5.6% H_2O ; and 68.1% H_2 , 23.4% CO , 3.39% CO_2 , and 5.03% H_2O . Emphasis on this work was placed, however, on the low Btu fuels corresponding to coal gasification.

The potential of the working electrode was controlled by a Wenking-Model 66TSI potentiostat. Steady-state currents were recorded on a Hewlett-Packard 7046A X-Y recorder. To eliminate errors caused by mass-transfer effects, transient potentiostatic techniques were employed using a Wenking ST72 potentiostat. This

instrument has a risetime of about 7 μ s when a step voltage is applied. A Tacussel type GSTP2B pulse-sweep generator was used to control this potentiostat with the output voltage being monitored with a Fluke Type 8020A digital voltmeter. Signals from the transient techniques were displayed and photographed on a Tektronix Type 547 oscilloscope. The recordings were performed with appropriate IR compensation using a feedback circuit. A furnace with a Lindberg-Hevi-Duty BPC Type 59344 temperature control was used to heat the half-cell. The temperature of the melt was monitored with an alumina-sheathed chromel-alumel thermocouple.

RESULTS AND DISCUSSION

To determine the effect of sulfur-containing fuels on the electrochemical performance of nickel and cobalt anodes, both steady-state and potential-step type measurements were performed in an electrochemical half-cell. Steady-state techniques were used to identify the enhanced currents caused by anodic sulfidation reactions and changes that may occur in the open-circuit potential as a result of such reactions. Figures 1 and 2 compare steady-state polarization curves for nickel and cobalt anodes in low-Btu fuel with and without 50 ppm H_2S . In both cases, introduction of sulfur as H_2S into the fuel was observed to perturb the open-circuit potential.

In the case of nickel (Figure 1) the shift was 15 mV positive of the initial -1154 mV open-circuit potential, whereas in the case of cobalt (Figure 2), the shift was very slightly in the cathodic direction by around 7 mV. Other than these minor shifts in the open-circuit potential, the current voltage characteristics are very similar in each case.

In the fuel cell, sulfur can be expected to enter the cathode as SO_2 where it will form sulfate. It would then be available for migration to the anode, where it could be reduced to sulfide species under the reducing conditions present. This could result in locally high accumulations of sulfide in the proximity of the anode. Consequently, H_2S introduced at concentrations of around 50 ppm with low-Btu fuel in the half-cell may not simulate the local high-sulfur content that may occur in the real fuel cell. This was probably responsible for the erratic open-circuit potential readings obtained at both nickel and cobalt anodes, which may be speculated to be either a mixed potential

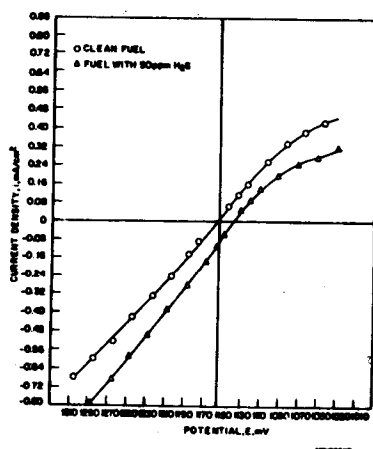


Figure 1. STEADY-STATE POLARIZATION CURVES FOR NICKEL USING LOW-Btu FUEL WITH AND WITHOUT 50 ppm H_2S ADDED (Li/K Electrolyte, 650°C)

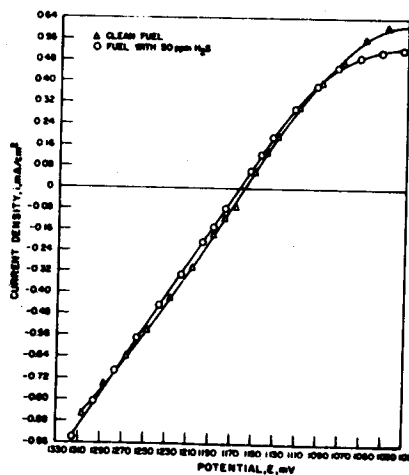


Figure 2. STEADY-STATE POLARIZATION CURVES FOR COBALT USING LOW-Btu FUEL WITH AND WITHOUT 50 ppm H_2S ADDED (Li/K Electrolyte, 650°C)

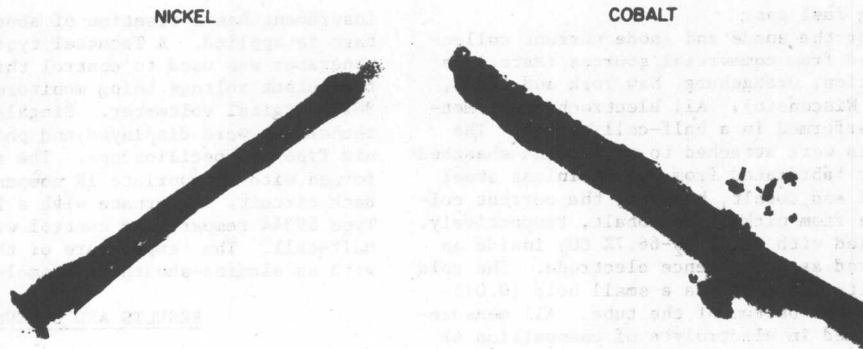


Figure 3. ANODES FROM
ELECTROCHEMICAL HALF-CELL AFTER
POTENTIOSTATTING IN
Li/K CARBONATE MELT IN
LOW-Btu FUEL CONTAINING 1000 ppm
H₂S AT 650°C

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effect caused by the formation of possible metal sulfide species on each anodes or due to some subtle changes in the fuel composition from one measurement to another.

The effect of higher sulfur concentrations on both the open-circuit potential and electrochemistry of nickel and cobalt anodes was evaluated using H₂S concentrations of approximately 1000 ppm. Steadystate polarization data on nickel and cobalt anodes in low-Btu fuel containing around 1000 ppm H₂S gave significantly enhanced anodic currents compared to clean fuel or that containing 50 ppm H₂S. Upon removal from the half-cell, evidence of extensive sulfidation on each of these electrodes was observed as shown in Fig. 3. In each case, the open-circuit potential was observed to be shifted to more negative values, possibly indicating a mixed-potential effect caused by the fuel oxidation reaction and the presence of metal sulfide on the anode surface. For nickel at 650°C (in low-Btu fuel), the open-circuit potential was shifted from -1154 to -1185 mV and for cobalt the shift was -1160 mV to -1200 mV. Clearly, neither of these two anode materials can be expected to be stable at such high-sulfur levels.

Potential step techniques were used to compare electrode kinetics in clean and sulfur-containing fuel. With the electrochemical conditions present in the half-cell, the rate of the overall electrochemical reaction was found to be dependent upon not only fuel bubbling rate, but also on the voltage sweep rate used. Such observations indicated diffusion or mixed control. To assess the impact of introducing sulfur species into the electrolyte from the fuel, it was of interest therefore to compare the electrode kinetics for both nickel and cobalt with clean and sulfur-containing fuels to indicate if any electrocatalytic poisoning effects occurred by the introduction of such sulfur impurities. Transient potentiostatic measurements (5,6) were performed for the separation of kinetic data under the probable mixed control condition present in the half-cell. This technique involved applying a voltage step to the nickel or cobalt working electrode and recording the current as a function of time. Under such conditions of mixed or diffusion control, the assumption was made that at time zero, only activation control will be present, that is, sufficient supply of electroactive species will be present together with minimal reaction products, so that any mass transfer effects will be minimized. Figure 4 shows a typical oscillogram for nickel with and without 50 ppm H₂S in low-Btu fuel. The kinetic current $i(0)$ value was found to be around 25 mA/cm² in both cases, indicating that such low levels of sulfur (50 ppm H₂S) appear to

have little effect upon the electrode kinetics for fuel oxidation, in essential agreement with the steadystate data.

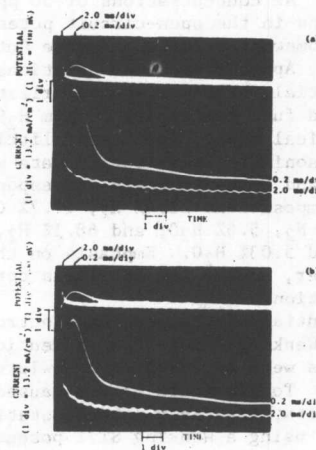


Figure 4. TRANSIENT
POTENTIOSTATIC MEASUREMENTS ON
NICKEL IN LITHIUM-POTASSIUM MELT
AT 650°C (Low-Btu Fuel Used Both
With (a) and Without (b) 50 ppm
H₂S Introduced With Fuel)

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A series of progressively more anodic and cathodic potential steps were applied to both nickel and cobalt in fuel with and without 50 ppm H₂S introduced into low-Btu fuel at 650°C. The respective activation polarization curves for these two anodes are shown in Figures 5 and 6, where they are compared with such data obtained using clean fuel. As was indicated earlier, 50 ppm H₂S does not appear to drastically poison the electrode kinetics for either the anodic or cathodic processes, although some small lowering in electrode activity does become apparent at higher applied overpotentials. Upon introduction of 50 ppm H₂S, the exchange current density was observed to become slightly lower, reducing from 26 to 25 mA/cm², and from 19.5 to 18.5 mA/cm², respectively, for nickel and cobalt, although such small variations in kinetic data can be considered to be well within the experimental error of this work. When potential step techniques are performed on these anode materials in fuel containing 1000 ppm H₂S anodic and cathodic cur-

rents appear to be dominated by the sulfidation reaction.

On the basis of this data, when high sulfide concentrations build up in the proximity of the anode, either directly from sulfurcontaining fuel or indirectly from SO_2 introduced into the cathode, neither nickel or cobalt appear to be viable candidates. Considerable incentive exists to identify potentially sulfur-tolerant anode materials for this fuel cell system.

Preliminary corrosion results for selected sulfur-tolerant candidate anodes are shown in Table I. Materials which showed apparent stability in this corrosion

test were then subjected to steady-state potentiostatic polarization evaluation in the electrochemical half-cell. These results are summarized in Table 2 where open-circuit potentials and anodic currents at 50 mV overpotential are compared.

Apart from nickel and cobalt anodes, which have already been discussed, highest stabilities were found for $\text{Mg}_{0.05}\text{La}_{0.95}\text{CrO}_3$ and TiC . Figure 7 compares steady-state polarization data on $\text{Mg}_{0.05}\text{La}_{0.95}\text{CrO}_3$ in low-Btu fuel with and without 50 ppm H_2S . No shift in the open-circuit potential was observed, and current voltage characteristics were very similar in both cases;

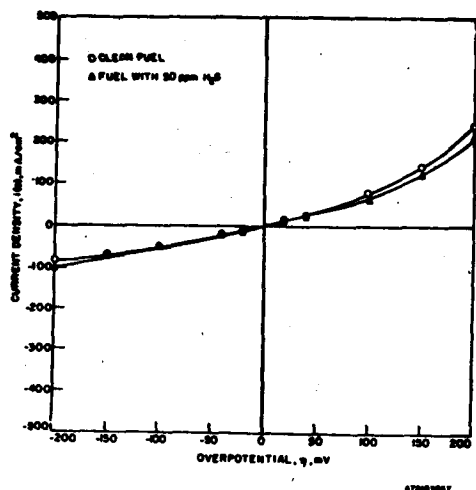


Figure 5. COMPARISON OF ACTIVATION POLARIZATION CURVES FOR NICKEL IN LOW-Btu FUEL THAT IS CLEAN AND IN FUEL WITH 50 ppm H_2S ADDED (Li/K Electrolyte, 650°C)

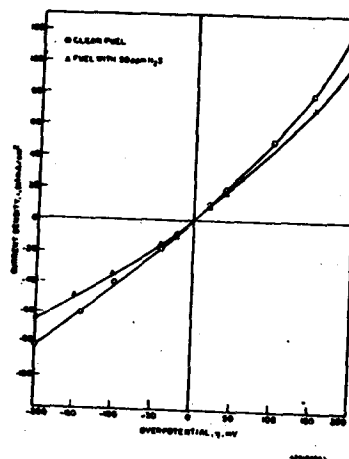


Figure 6. COMPARISON OF ACTIVATION POLARIZATION CURVES FOR COBALT IN LOW-Btu FUEL THAT IS CLEAN AND IN FUEL WITH 50 ppm H_2S ADDED

Table 1. CORROSION RESULTS FOR CANDIDATE ANODE MATERIALS

Composition, %	Total Exposure to Low-Btu Fuel, hr	Period in H_2S (274 ppm), hr	Total Weight Change, %	Comments
WC-10; CO-90	1588	1301	- 3.3	
TaC	1122	1122	--	Completely corroded.
TiB_2	432	432	--	Completely corroded.
ZrC	168	none	--	Completely corroded.
TiC	1506	1051	- 1.0	
VC	355	187	-24.7	
NbN	1506	1051	+10.1	
$\text{Mg}_{0.05}\text{La}_{0.95}\text{CrO}_3$	1506	1051	+ 0.1	
TiO_2 (Ta-doped)	1343	1080	+ 0.7	
TiO_2 (Nb-doped)	1343	1080	- 1.1	
Mo-90; Ti-10	1080	1080	-32.4	
Co-64.8; Mo-35.2	1554	1554	-27.8	
Co-38.1; Mo-61.9	432	432	-53.2	
Nickel	1554	1554	- 0.9	
Fe-90.0 Cr-9.0; Mo-1.0	432	432	-48.5	
Cr-30.6; Co-69.4	648	648	--	Completely corroded.
Co-49; Si-W	648	648	--	Completely corroded.
Co-24.3; 75.7-W	648	648	--	Completely corroded.
Co-63.0; Cr-30.0; Mo-7.0	1122	1122	--	Completely corroded.
Co-22.1; Cr-77.9	1122	1122	--	Completely corroded.
Cobalt	1122	1122	+13.7	
Cr_2O_3 (1 mole TiO_2)	1122	1122	+ 0.3	
Tungsten	1122	1122	+ 7.0	Sample broken.
Molybdenum	1122	1122	-44.7	
FeB	474	474	--	Completely corroded.
Ni-50; Co-50	474	474	--	Completely corroded.
CoP5	474	474	+ 3.5	
WS_2	474	474	--	Completely corroded.
CoP3	474	474	--	Completely corroded.
Ni-50; Al-50	474	474	--	Completely corroded.
CoAs2	474	474	+25.9	
MoS_2	474	474	+ 0.9	
Cr_3Co_2	474	474	--	Completely corroded.
WC	648	648	--	Completely corroded.
MnS	648	648	--	Completely corroded.
			-27.0	Sample broken.

Table 2. POTENTIOSTATIC EVALUATION OF ANODE MATERIALS USING LOW-BTU FUEL GAS IN BINARY CARBONATE MELT AT 650°C

Composition, %	Clean Fuel		Fuel with 50 ppm H ₂ S		Comments
	Open Circuit Potential, mV	Current i (at 50 mV from rest potential) mA/cm ²	Open Circuit Potential, mV	Current i (at 50 mV from rest potential) mA/cm ²	
Cr ₂ O ₃ -99; TiO ₂ -1	-1032	0.122			Electrode badly eroded. Trace of current very noisy. Indicates corrosion; not run cathodically. Electrode Corroded; not run in H ₂ S.
Nickel-50; Cobalt-50	-1138	0.381	-1102	0.202	
Tungsten Carbide	-1368	2.918	-1305	1.134	
Tungsten Cobalt	-1402	2.299			Electrode corroded; not run in H ₂ S.
Titanium Carbide	-1142*	0.166*	-1135	0.167	
Mg _{0.05} La _{0.95} CrO ₃ ; Ni-50; Al-50	-1130	0.040	-1132	0.041	
	-1160	0.918			Very large cathodic current.
TiO ₂ (Ta doped)	-1097	0.114	-1106**	0.157**	
TiO ₂ (Nb doped)	-1154	0.250	-1134**	0.105**	
Nickel			-1141	0.193	Indicates corrosion
Nickel			-1185**	17.51**	
Cobalt	-1138	0.304	-1163	0.304	
Cobalt			-1201**	8.47**	Indicates corrosion; not run in H ₂ S. No anodic current.
Niobium Nitride	-1104	0.493			
Chromium-77.9; Cobalt-22.1	-1290	0.0			
CoAs ₂	-1136	0.32			

* High-Btu fuel.

** 1000 ppm H₂S.

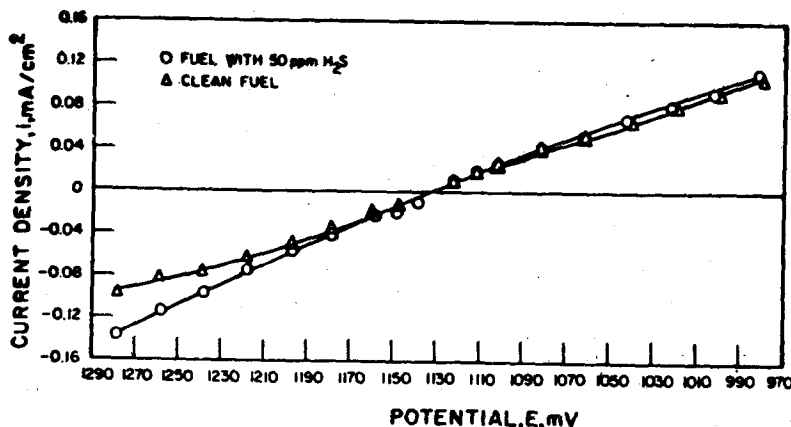


Figure 7. STEADY-STATE POLARIZATION CURVE FOR Mg_{0.05}La_{0.95}CrO₃ USING LOW-Btu FUEL WITH AND WITHOUT 50 ppm H₂S ADDED (Li/K Electrolyte, 650°C)

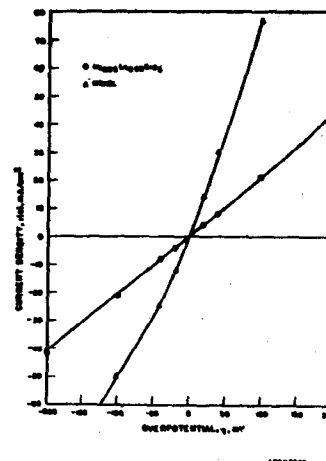


Figure 8. ACTIVATION POLARIZATION CURVE FOR Mg_{0.05}La_{0.95}CrO₃ AND NICKEL USING LOW-Btu FUEL (Li/K Carbonate Electrolyte, 650°C)

particularly in the anodic region. Introduction of fuel containing 1000 ppm of H₂S did not shift the open-circuit potential to negative values as observed with nickel and cobalt anodes. Examination of this material afterwards indicated no surface corrosion even after prolonged anodic potentiostating.

Figure 8 compares activation data performed on this material using the potential step technique with that obtained for nickel. For Mg_{0.05}La_{0.95}CrO₃ exchange current densities of around 8 mA/cm² were obtained in low-Btu fuel. Although considerably faster kinetics can be observed with the nickel anode, the exchange current density at the Mg_{0.05}La_{0.95}CrO₃ electrode is still rapid enough to expect mass transfer control for the fuel oxidation process.

Consequently from the kinetic data and apparently high-sulfur tolerance of Mg_{0.05}La_{0.95}CrO₃, this material is an interesting candidate for a sulfur-tolerant anode. However, comparison of steady-state potentiostatic data obtained with Mg_{0.05}La_{0.95}CrO₃ and nickel in

clean electrolyte showed lower currents for the chromium. Because both electrodes exhibited rapid electrode kinetics, the smaller currents observed with Mg_{0.05}La_{0.95}CrO₃ in comparison with nickel may be due either to more local hinderance by the diffusion of reaction products away from the electrode surface or caused by differences in the electrolyte stirring rates in the two experiments.

Steady-state polarization measurements have been respectively performed on TiC, Cr₂O₃ (1 mole percent of TiO₂), WCo (W - 75.7%, Co - 24.3%), nichrome (80% Ni, 20% Cr), and NiAl all in the lithium/potassium carbonate electrolyte at 650°C in low-Btu fuel. Upon examination of all of these materials, evidence of surface corrosion became evident. Candidate anode current collector materials were subjected to an initial screening conversion test as described previously for the selected anodes. The materials selected, together with the corrosion results, are shown in Table 3. From these results, good corrosion stability was found for 446 and

Table 3. CORROSION RESULTS FOR CANDIDATE ANODE CURRENT COLLECTOR MATERIALS

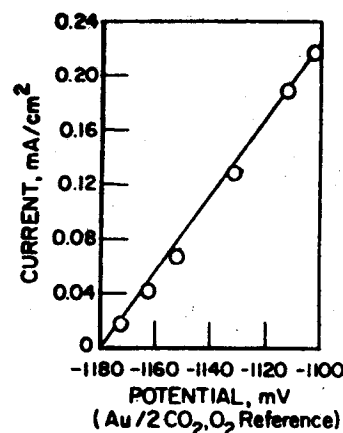
Composition, %	Total Exposure to Low-Btu Fuel, hr	Period in H ₂ S (274 ppm), hr	Total Weight Change, %	Comments
C-0.25; Mn-2.0; Si-1.5; Cr-25.0; Ni-20; Fe-51.25 (SS-310)	1588	1301	+ 0.2	
Cr-50.0; Ni-49.0; Ti-1.0 (UNILOY)	1588	1301	+ 0.5	
Co-50.0; Cr-28.0; Fe-16.5; W-5.5	355	187	-20.3	
Fe-81.8; Al-15; Mo-3.2 (VE-441)	648	648	+82.9	
Cr-21.0; Mn-9.0; Ni-6.0; Fe-64	1588	1301	+ 0.5	
Fe-70; Al-10; Mn-20 (EX-20)	648	648	+26.7	
C-0.2; Cr-25.0; Ni-0.5; Fe-74.3 (SS-446)	1588	1301	+ 0.6	
Cr-22.0; Co-0.5; Al-5.0; Fe-73.5 (KANTHAL)	258	258	--	Completely corroded.
C-0.15; Mn-2.0; Si-1.0; P-0.2; S-0.15; Cr-18.0; Ni-9.0; Mo-0.6; Fe-Bal. (SS-303)	1554	1554	- 5.3	
C-0.08; Cr-17.0; Ni-12; Mo-3.0; Fe-Bal. (SS-316)	1554	1554	+ 2.2	

310 stainless steels, together with Uniloy. More promising materials were subjected to steady-state potentiostatic evaluation. Figure 9 shows the steady-state current voltage characteristics obtained with 446 stainless steel. The results of such potentiostatic testing for the selected anode current collector materials are summarized in Table 4. Materials were anodically potentiostatted at 75 mV in low-Btu fuel with and without H₂S and the currents recorded as a function of time. A decay in current with time was taken as indicative of surface oxide formation as shown in Figure 10 for 446 stainless steel. Of those materials evaluated, high stabilities were found for 410 and 310 stainless steels. Open-circuit potentials found for the stainless steels in low-Btu fuel were fairly close to those expected; nevertheless some of the other candidates that readily corroded showed somewhat more cathodic potentials.

CONCLUSIONS

At low-sulfur concentrations (≈ 50 ppm) the electrode kinetics for fuel oxidation on both nickel and cobalt anodes do not appear to be poisoned. At high-sulfur concentrations (≈ 1000 ppm) shifts in the open-circuit potential of both these materials occurred together with evidence of sulfidation.

Promising anode materials which may show long-term sulfur tolerance include $\text{Mg}_{0.05}\text{La}_{0.95}\text{CrO}_3$ and TiC. However, their long-term performance as porous sintered anodes has yet to be evaluated. Anode current collectors showing high stability have been found to include 410 and 310 stainless steels.



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Figure 9. STEADY-STATE POLARIZATION CURVE FOR 446 STAINLESS STEEL IN LOW-Btu FUEL AT 650°C

Table 4. POTENTIOSTATIC EVALUATION OF ANODE CURRENT COLLECTOR MATERIALS USING LOW-BTU FUEL GAS IN BINARY CARBONATE MELT AT 650°C

Composition, %	Clean Fuel		Fuel with 50 ppm H ₂ S		Comments
	Open Circuit Potential, mV	Current i (at 50 mV from rest potential) mA/cm ²	Open Circuit Potential, mV	Current i (at 50 mV from rest potential) mA/cm ²	
C-0.2; Cr-25.0; Ni-0.5; Fe-74.3 (SS 446)	-1182	0.128	-1137	0.147	
C-0.25; Mn-2.0; Si-1.5; Cr-25.0; Ni-20; Fe-51.25 (SS 310)	-1186	0.063	-1145	0.089	Black coating after test.
C-0.08; Cr-17.0; Ni-12.0; Mo-3.0; Fe-Bal (SS 316)	-1173	0.156	-1164	0.197	Black coating after test.
C-0.15; Mn-1.0; Si-1.0; Cr-12.5; Fe-Bal (SS 410)	-1173	0.184	-1148	0.157	
C-0.15; Mn-1.0; Si-1.0; Ni-45.45; Fe-18.5; Cr-21.8; Co-2.5; Mo-9.0; W-0.6 (Hastalloy X)	-1167	0.236	-1147	0.207	
Ni-80.0; Cr-20.0 (nichrome)	-1257	3.508			Corroded
Cr-22.0; Co-0.5; Al-5.0; Fe-73.5 (Kanthal)	-1330	0.0			Corroded
Fe-70; Al-10; Mn-20 (Ex 20)	-1347	0.218	-1222	0.911	
Fe-81.8; Al-15.0; Mo-3.2 (VE 441)	-1382	0.413			Crusted with thick black oxide.