Co-generation of Carbon-Free Hydrogen and Electricity from Coal in a Steam-Carbon Fuel Cell with Carbon Capture

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Abstract
This project based on a novel fuel cell concept collectively aims to address three aspects of energy production and storage using coal, namely advanced coal conversion in a specialized fuel cell, electrochemical hydrogen production from coal for energy storage, and CO₂ mitigation and capture without separation, all achieved in a single process chamber and without the need for external power from the grid. In other words, it strives to develop a clean coal technology that simultaneously generates electric power, stores part of coal’s energy in clean hydrogen fuel, and produces nearly capture-ready CO₂. If successful and widely adopted, this technology promises to double the efficiency of coal power generation, resulting in a significant reduction in global CO₂ emissions thereby ensuring continued use of our cheapest and most abundant fuel – coal – in an environmentally friendly manner.

The steam-carbon fuel cell concept introduced in this project allows spontaneous conversion of coal into an environmentally benign fuel, hydrogen. This novel concept not only achieves steam gasification of coal while keeping hydrogen and carbon dioxide product streams unmixed and physically separated, but more importantly, drives the otherwise thermodynamically uphill reaction for steam dissociation energetically downhill. In this process scheme, no nitrogen enters the reaction stream so the anode product gases contain primarily CO₂ and unreacted CO, while the cathode gas stream contains primarily H₂ and unreacted steam. In other words, the steam-carbon fuel cell concept enables simultaneous and spontaneous production of carbon-free hydrogen and electricity from coal (or biomass) and produces a highly concentrated CO₂ product stream that can easily be captured.

Work in our laboratory over the past year has focused in building the research team and physical facilities necessary for assembly and testing of various fuel cell membrane electrode assemblies (MEAs) of different catalysts compositions, particularly the testing of sulfur tolerant anode materials. As sulfur is a major coal contaminant and a barrier to advance this technology, this project also aims to develop sorbent materials for capture and removal of coal contaminants, mainly sulfur so screening is essential to the success of the project. Furthermore, work has begun on the synthesis of prospective catalysts that are reported to show good sulfur tolerance under conditions relevant to carbon fuel cells. We report the preliminary results of our synthesis efforts for sulfur tolerant anode materials. We are in the process of screening potential candidates for sulfur tolerant anode materials, assessing their performance and potential for this project, as well as synthesis and testing of candidates for solid sorbents. Finally, over the previous year we have successfully expanded our modeling work to demonstrate and quantify the effects from conductive, convective, and radiative heat transfer in carbon fuel cells. This advance in the modeling work has helped to more completely describe the different parameters relevant to predicting fuel cell performance, and serves as a starting point in
expanding the model to account for the elementary rate processes at the membrane electrode assembly itself.

Introduction

This project aims to develop a clean coal technology that simultaneously generates electric power, stores part of coal’s energy in clean hydrogen fuel, and produces nearly capture-ready CO$_2$. Storing coal energy in the environmentally benign fuel hydrogen is an attractive proposition. As a clean energy carrier, hydrogen has the potential to become a significant player especially in the transportation sector. Molecular hydrogen, found only in trace quantities in nature, must be synthesized from hydrogen-containing compounds such as water or hydrocarbons. The production of hydrogen by steam reforming is a mature technology that accounts for more than 75% of the current production capacity, but is cost effective only when it is produced centrally and at large scale. Storage and transportation of hydrogen, however, is costly and inefficient because of its low volumetric energy density (~11 MJ/m$^3$). That is why distributed generation is important and why the development of novel H$_2$ synthesis processes with low energy consumption and minimum greenhouse gas emissions is critically needed. If an effective hydrogen-based clean transportation economy is to be developed, then distributed production of hydrogen from coal is a viable low-cost option. Development efforts by major automobile manufacturers towards fuel cell driven vehicles, if commercially successful, necessitates parallel efforts in developing cost effective technologies for distributed production of carbon-free hydrogen.

The scheme used in this project is built upon the steam-carbon fuel cell concept [1-4] and involves conversion of coal or biomass at the anode, while hydrogen from the reduction of steam is produced at the cathode, shown in Fig. 1. The two reaction systems at the anode and cathode are separated physically by an impermeable oxide ion conducting ceramic membrane. This scheme in essence allows the water gas shift and steam gasification reactions of coal to be achieved in such a way that the anode and cathode reaction streams do not mix with each other, minimizing entropic losses. Furthermore, the favorable thermodynamics of this system allows spontaneous and simultaneous production of hydrogen and electrical energy. The downhill driving force facilitates a large difference in the chemical potential for oxygen across the ceramic membrane, whereby oxygen is abstracted from steam at the cathode, transported via vacancy mechanism across the crystal lattice of the membrane towards the anode where it reacts with the carbonaceous fuel.[5] The electrons released at the anode travel through the external circuit to perform useful electrical work. This novel scheme offers efficient and cost-effective production of carbon-free hydrogen and electrical power.

The goal of the project is to gain mechanistic and operational understanding of this novel fuel cell concept, which represents a game-changing opportunity to achieve highly efficient conversion of coal and biomass in fuel cells on practical scales with simultaneous and spontaneous production of electricity and carbon-free hydrogen. This research effort involves experimental, materials, and modeling components. Laboratory experiments are designed to provide the information needed to characterize mass transport and electrochemistry at the cathode and anode of the steam-carbon fuel cell as well the heterogeneous gasification reactions that occur in the coal bed, producing the synthesis gas that is oxidized at the anode. Catalytic materials will be investigated for
improving electrode kinetics at the anode and cathode, while materials strategies will be
developed to address the deleterious effects of coal contaminants, primarily sulfur.
Models developed to describe the observed phenomena will be implemented to gain
fundamental understanding in the areas of coal gasification, carbon monoxide
electrochemistry and steam electrolysis. System optimization will also be an aspect of the
continuing research. Understanding challenges in system scaling, thermal management,
power management, and membrane electrode assembly designs, especially for multi-cell
configurations are key concerns. If successful and widely adopted, the technology would
greatly reduce greenhouse gas emissions during efficient production of high-purity
hydrogen and electricity from coal and biomass.

Figure 1: Schematic of a coupled steam-carbon and air-carbon fuel cell,
and the corresponding oxygen chemical potential profile across the
coupled cell.

The impacts of this research project are in the areas of efficient energy conversion
(coal) and storage (hydrogen) with reduced carbon footprint, as well as in the education
of students in advanced approaches to energy and environment for a sustainable future.

Background

Currently, conventional room temperature electrolysis of water is the only
commercial technology available for distributed generation of hydrogen. But
thermodynamically this is steeply an uphill process and hence is energy intensive. An
external bias of about 1.8 - 2 V that opposes and is significantly greater than the open
circuit voltage of 1.23 V must be applied to the cell in order to break the O-H bonds in
water, permitting the formation of the H-H bond. In other words, 60% to 70% of the
electricity used in conventional water electrolysis schemes is consumed merely to
overcome this potential barrier and overdrive the cell uphill. This reduces the efficiency
and renders electrolysis an inefficient, costly and electricity intensive process for
distributed hydrogen production. Considering that nearly 50% of the global grid power is
generated primarily by coal fired plants operating at conversion efficiencies in the low 30% range, the overall efficiency of conventional water (or, steam) electrolysis is further reduced significantly by this efficiency multiplier.

The fuel cell scheme adopted in this project for hydrogen production is different from and much superior to conventional electrolysis, and is expected to be nearly two times more efficient. More importantly, it will be entirely free of grid electricity otherwise needed for electrolysis. In this innovative scheme, H$_2$O dissociation and fuel (i.e., carbon) oxidation processes are coupled and the resulting net reaction is thermodynamically downhill. In other words, the dissociation reaction for steam occurs spontaneously. So no electricity from the external power grid is required or needed, which results in big savings in electrical energy consumption. Moreover, the cell operates at high temperatures where the open circuit potential for steam dissociation is lower (0.9 V for water at 1200 K versus 1.23 V for water at room temperature), and electrode kinetics and fluxes are much faster. Indeed, Doenitz et al. [6] have demonstrated steam electrolysis using a solid oxide electrolyzer at applied biases in excess of 0.9 V in the range 900 – 1000°C.

The coupled fuel cell scheme is inherently suitable for large-scale applications. A 25 kW scale solid oxide fuel cell power plant is under development by the industrial teams in the U.S. Department of Energy’s Solid State Energy Conversion Alliance (SECA) program and 2 - 5 kW level power units have already been tested.[7] Estimates indicate higher efficiency and significant benefits in capital cost and cost of electricity when integrated gasification fuel cell technology is compared to other coal conversion technologies. Large-scale projects include DOE’s FutureGen 2.0 initiative and the GreenGen project in China. Also, Gür et al. [8] have achieved practical power densities up to 450 mW/cm$^2$ at 0.64 V and 850 °C using untreated Alaska coal char in a fluidized bed carbon fuel cell, similarly operating under the same basic principle as studied here. Furthermore, Gür and co-workers have demonstrated successful operation of a 50-cell stack running on CO fuel and providing nearly 1.2 kW of power or 224 mW/cm$^2$ power density at 800 °C.[9] Recently, we have demonstrated the fluidized-bed carbon fuel cell (FB-CFC) in which a tubular solid oxide fuel cell (SOFC) is immersed in a bed of carbon particles.[5, 10] In another configuration involving flat button-cell geometry, current densities as high as 275 mA/cm$^2$ at 0.516 V (maximum power: 142 mW/cm$^2$) were realized at 900 °C.[11]

But a major challenge in realizing coal-powered fuel cells is over-coming sulfur poisoning issues of the anode catalyst. Many studies have cited the substantial loss in performance of a nickel-based anodes for CO oxidation, with losses in power density as high as 60 % reported, making nickel based catalysts unsuited for applications where sulfur is present.[12, 13] As such, it is necessary to explore alternative materials that have been proposed in the literature, as well as develop our own. It is not sufficient, however, to accept the sulfur tolerance of these materials at face value. Some studies have highlighted excellent sulfur tolerance only in the presence of hydrogen, [14-21] and of the few studies that examined sulfur tolerance in hydrogen-free feed gases, all have shown substantially higher losses in CO versus hydrogen, [22] possible due to the ability of hydrogen to regenerate these catalysts.[16, 17] In terms of sulfur tolerance and ease of synthesis, perovskites have shown the greatest promise at improving the sulfur tolerance.
of solid oxide fuel cells. Judicious choice of dopants can be used to improve both of the
electronic and ionic conductivity perovskites, but much debate remains over the
importance of these parameters. For example, independent work by Armstrong [23] and
Kilner [24, 25] showed that in some perovskites, the rate of surface exchange of oxygen
is the rate limiting step for ionic transport and not the ionic transport, stressing the
importance of tuning the surface properties of perovskites to improve their catalytic
performance. Furthermore, while many groups have reported the conductivity of their
synthesized perovskites, there are several cases where the performance of the perovskite
has not followed expected trends in ionic or electronic conductivity. Perhaps one of the
few consistencies in the literature is the improvement in performance of Fe, Mo, and Co
doped perovskites under sulfurous conditions, and in the case of Mo, is believed to be
due to the onset of an electronically conductive MoS$_2$ phase. As such, more focus should
be directed towards materials known to show improved performance after hydrogen
sulfide exposure rather than those with improved conductivities.

The modeling aspect of this report builds upon our previously reported model [26] for
a planar SO-CFC, and is further expanded to account for heat transfer effects throughout
the cell that also contains a bed of solid carbonaceous fuel. This is necessary in order to
understand and control the thermal gradients within the cell that may affect cell
efficiency and performance through such factors as gasification rates of the carbon fuel as
well as rates of the electrochemical half-cell reactions. While prior modeling studies on
solid oxide fuel cells (SOFC) include both tubular [27-31] and planar [32-44] cell
geometries with heat transfer, these models considered primarily cells that utilized
gaseous fuels, typically hydrogen, or syngas derived from internal reforming of methane.
Furthermore, only a select few of these studies include radiation effects.[31, 37, 39, 40,
43] Bessette et al. [31] verified their tubular model with data from Westinghouse, and
indicated that radiation between solid surfaces is a major mode of heat transfer.
Accordingly, we have developed a comprehensive approach to heat transfer that includes
radiation effects as well as conduction and convection as part of our modeling effort to
fully understand the extent of heat transfer effects in SO-CFCs.

However, the solid carbon bed in the anode chamber of our SO-CFC presents
challenges for modeling heat transfer through a porous solid medium. Previous studies
have considered conduction through porous electrodes by using a simple weighted
average of the gas phase and solid phase conductivities.[32, 33, 44] The present study
expands beyond the earlier work and takes into account the thermal gradients in the
carbon bed that result from conduction, convection, and radiation by using an effective
thermal conductivity derived for heat transfer through porous, unconsolidated solids.[45]

**Results**

*Experimental Studies*

Much of the experimental work for this project focuses on characterizing anode and
cathode catalysts for fuel cells under normal operating conditions, so we built several test
stands for characterizing fuel cells. The general schematic of the test setup for each stand
is shown in Fig. 2. For the cathode compartment, only purge nitrogen and air are
available and their flow rates are controlled through the use of rotameters. For the anode
compartment, rotameters control the flow rates of a nitrogen purge and diluent gas,
hydrogen for catalyst reduction, and a CO/N$_2$ mixture for studying CO kinetics. For
sulfur tolerant anode testing, an additional rotameter metering the flow of \( \text{H}_2\text{S}/\text{N}_2 \) is also present. For the anode compartment, the purge and diluent \( \text{N}_2 \) is used for controlling the partial pressures of CO, H\(_2\), and H\(_2\)S so that the effects of concentration of these reagents can be examined using electrochemical impedance spectrum (EIS) measurements. For the fuel cell itself, the membrane electrode assembly (MEA), consisting of an anode catalysts adhered to an ionically conductive electrolyte such as yttrium stabilized zirconia (YSZ) with a cathode catalyst adhered to the other side, is placed between two silver rings attached to electrical leads. The silver rings serve two purposes. First, they serve as current collectors for the anode and cathode catalysts allowing electrochemical characterization of the anode and cathode catalysts. Second, silver serves as a means of sealing the MEA gas-tight between alumina tubes, which serve as the anode and cathode gas compartments. We chose silver as the sealant of choice as silver becomes malleable and provides a gas-tight seal at fuel cell temperatures, and also is inexpensive. Above 920 °C, the vapor pressure of silver becomes significant, and expensive gold current collectors must then be used. The anode electrode, shown in green, contains an electrocatalyst, which may or may not be supported on an ionically conductive material. For the commercial MEA, this layer is composed of nickel supported on gadolinium-doped cerium (GDC) and YSZ. Similarly, the cathode electrode, shown in red, also consists of catalyst that may or may not be supported on an ionically conductive material. For the commercial MEA, the cathode is \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) (LSM) supported on GDC. A picture of one of the test stands with on-line GC is shown in Fig. 3.

**Figure 2:** Flow diagram of a typical test stand. The flow rate of each gas to the anode and cathode compartments is controlled with rotameters. Anode exhaust gases are passed through a gas chromatograph after passing over the anode electrode for composition analysis. The fuel cell itself (enlarged) is a membrane electrode assembly (MEA) compressed between two alumina tubes with silver (Ag) current collectors in contact with the electrode layer to provide electrical contract with the fuel cell catalysts as well as provide a seal between the MEA and the alumina tubes.
Figure 3: One of the test stands with on-line GC-analysis. There are currently two test stands in our lab with this capability, and a third test stand is under construction.

The above schematic provides a means for testing the effects of temperature, gas composition, gas flow rate, and MEA composition on fuel cell performance. By varying temperature, Arrhenius activation energies for anode and cathode processes can be extracted. By varying gas composition and flow rates, it is possible to more accurately identify the different components of the acquired electrochemical impedance spectra, as well as introduce or remove bulk gas transport effects for a more complete analysis of the MEA performance. Finally, the above scheme allows for efficient screening of MEA compositions, such as varying anode or cathode electrocatalysts or microstructure, as MEAs can be easily inserted and removed from between the two anode and cathode compartments. This would be in contrast to cementing the MEA to the end of an alumina tube, which our group has done previously, [26]. As a result, our group has begun to test fuel cells, establishing baseline fuel cell measurements.

For baseline fuel cell characterization, a commercial Ni-GDC/Ni-YSZ/Hionic™/LSM/LSM-GDC (Ni/LSM) button cell from NextCell™ has been characterized to benchmark all electrochemical measurements and fuel cell performance tests. Because this fuel cell is commercially available from an independent source, other research groups attempting to duplicate our research as a means of verifying our results can use it. The Ni/LSM cell was characterized both with hydrogen and with carbon monoxide as a fuel to provide a baseline for future cells to a commercially viable fuel cell. While the data shown in Fig. 4 comes from a single cell, the CO/Air system was studied after several hours of studying the H₂/Air system at different temperatures, so there were changes in the cell resistance due to cell characterization. Electrochemical impedance measurements and current-voltage curves were used to extract kinetic parameters of the fuel cell, such as activation energies for CO and hydrogen oxidation, as
well as to determine the charge transfer coefficients for both anode and cathode processes. A typical electrochemical impedance spectrum (EIS) for H\textsubscript{2}/Air and CO/air is shown in Fig. 4.

**Figure 4:** Typical electrochemical impedance spectra (EIS) of a Ni/LCSM fuel cell using (a) H\textsubscript{2}/Air at 1123 K (red) and CO/Air at 1123 K (blue), both operating near open circuit potential. The fit to the equivalent circuit is shown over each spectrum in black, with the different components or the equivalent circuit labeled. (b) H\textsubscript{2}/Air at 0.700 V and 1198 K with different H\textsubscript{2}/N\textsubscript{2} gas compositions in the anode compartment to determine which parts of the equivalent circuit were due to anode and cathode components. (c) Voltage (●) and power density (■) versus current density for the CO/Air system at three different temperatures.

Because of the rapid onset of carbon deposition at OCV on the catalytic Ni anode surface, EIS measurements were not conducted at open circuit voltage. Furthermore, it was undesirable to generate NiO through over-driving the H\textsubscript{2}/Air fuel cell. Hence, EIS measurements were avoided under OCV conditions. Under cell polarization, the oxygen
The impedance models were fit to a typical fuel cell model consisting of a stray inductor (due to leads), two parallel circuits consisting of a resistor and constant phase element (CPE) representing anode and cathode processes, and a series resistor representing the cell ohmic resistance. By varying the partial pressure of hydrogen in anode compartment, shown in Fig. 4b, we were able to determine which components of the EIS measurements correspond to anode and cathode kinetics and appropriately make assignments to the arcs shown in Fig. 3a. Consequentially, the second arc in Fig. 3a is attributed to hydrogen oxidation in the H\textsubscript{2}/Air cell, and due to similar resistances between the first arc of H\textsubscript{2}/Air and CO/Air cells, the first arc in Fig. 4a are attributed to oxygen reduction. Finally, the first intersection of the curve with the imaginary axis is attributed to the high frequency resistance (HFR), or more simply, the series resistance that corresponds to ohmic losses. The equivalent circuit is shown in Fig. 5. Additionally, both the voltage and power density are plotted against current density in Fig. 4c for the CO/Air system at three different temperatures.

Ni/YSZ is expected to perform reasonably well in very low sulfur environments as offered by most biomass, but does not have sufficient resiliency to sulfur poisoning in the case untreated coal is employed as the fuel. Accordingly, our group has been looking at alternative anode materials and synthesizing oxide-based catalytic anodes in order to ascertain the viability of these materials for the steam-carbon fuel cell. The Ni/YSZ catalyst is known to have poor tolerance to sulfur poisoning, losing up to 60 \% of its catalytic activity on exposure to H\textsubscript{2}S, [46] forming nickel-sulfide compounds. [47] A survey of the literature has shown that the perovskite anode materials show the most promise for sulfur tolerant anode materials, [48-51] particularly perturbations of the parent strontium titanate (SrTiO\textsubscript{3}) perovskite. As shown in Fig. 6, SrTiO\textsubscript{3} is one of the simplest perovskite structures, with strontium cations in the A positions located at the corners of the unit cell, and titanium in the B sites located in the center of the unit cell. The parent perovskite SrTiO\textsubscript{3} is a dielectric with negligible conductivity for electronic or

![Figure 5: Equivalent circuit used to model CO/Air fuel cells. A similar model substituting CO oxidation with H\textsubscript{2} oxidation was used with the H\textsubscript{2}/Air fuel cells.](image)
ionic species under atmospheric conditions, but it is a good matrix material to build the perovskite catalyst via designed doping. Doping of aliovalent cations in the A-site, \(i.e.,\) in place of Sr, is expected to alter oxygen non-stoichiometry that facilitates oxide ion transport through the perovskite lattice. Doping of multi-valent transition metals at the B-site promote electronic conductivity, which is necessary for an effective electrode material.

Accordingly, we have synthesized several compositions of yttrium doped strontium titanates, [52] particularly \(Y_{0.1}\)Sr\(_{0.9}\)TiO\(_3\) and \(Y_{0.2}\)Sr\(_{0.8}\)TiO\(_3\), which are known to show better anode performance than SrTiO\(_3\) alone. The rationale for their use is that they are known to have better ionic conductivities and sulfur tolerance. We have also synthesized perovskites that are intermediate compositions to known sulfur tolerant anode materials to investigate the effects of the dopants and better understand how each dopant plays a role in improving both CO oxidation and sulfur tolerance. In particular, the substitution of cations with labile oxidation states, such as Ti\((3/4)\) or V\((3/4)\) can be used to improve electronic conductivity by increasing the number of d-band electrons, and cationic differences in the A-site substitution, such as Y for Sr or La for Sr, can improve ionic conductivity.[53, 54] The results of these synthesis is expected to not only culminate in the synthesis and testing of perovskites that are known to show improvement under sulfurous conditions, such as lanthanum doped STO [16, 17] lanthanum-barium doped STO, [50, 55] and lanthanum-iron doped STO, [14] but also in the development of new novel sulfur tolerant anode materials. X-ray diffraction measurements of these materials verify a pure perovskite phase, as shown in Fig. 7. These are just some of the materials that have been synthesized to date.

![Figure 6: Four different perovskite materials used in solid oxide fuel cells, with 16 unit cells shown. (A) Strontium titanate (SrTiO\(_3\)), a well-known perovskite with poor performance but is being used as a good baseline for performance of perovskite materials.[56] (B) La\(_{1-x}\)Sr\(_x\)TiO\(_3\) titanate (LST), which gives better performance that STO with on 20 % performance loss in 100 ppm H\(_2\)S.[16, 17] (C) La\(_{1-x-y}\)Ba\(_x\)SrYTiO\(_3\), known to give improved performance with sulfur exposure.[50, 55] (D) La\(_{1-x}\)Sr\(_{1-x}\)Fe\(_x\)Cr\(_{1-x}\)O\(_3\), known to show improved performance on exposure to hydrogen sulfide.[14] Red=oxygen, blue=titanium, green=strontium, black=lanthanum, pink=barium, gold=iron, fuchsia=chromium.](image-url)
Figure 7: Powder X-ray diffraction pattern of the different perovskite materials synthesized for sulfur tolerance. Major reflections have been labeled for clarity.

We have also been using scanning electron microscopy (SEM) to accurately measure electrode thickness and verify porosity of the MEAs used in our studies. An SEM image of the commercially available Ni/LCSM is shown in Fig. 8 both (a) before and (b) after characterization. The electrolyte thickness ranges from 140 to 150 µm, with the anode and cathode catalyst layers circa 55 and 65 µm, respectively. Delamination of the catalyst is evident in Fig. 8b, whereby the anode catalyst layer has substantially thinned and flakes of the anode catalyst layer were observed when the MEA was removed from the test stand. This may be related to the insufficient porosity of the anode layer microstructure. At high polarization, this may lead to building up large discharge pressures for oxygen at the anode/electrolyte interface that eventually bursts and delaminates the two layers at the interface. This suggests that while the commercial catalyst gives moderate performance, it does suffer from unfavorable microstructure and poor electrode-electrolyte adhesion. We expect to overcome this difficulty by improving electrode morphology via controlled fabrication.

Figure 8: Scanning electron microscope (SEM) image of a membrane electrode assembly of the Ni/LCSM (a) before and (b) after characterization.
Computational Work

Our experimental efforts are complemented and augmented by modeling studies to simulate the impact of individual rate processes as well as the expected performance of our cells. In previous work in our lab, a finite-element model was developed to determine the interplay between overall cell efficiency, hydrogen production rate and electricity production.[26] This preliminary model accounted for mass transport both in cathode chambers and in the anode fuel bed, detailed carbon chemistry, as well as electrochemistry, but neglected energy transfer and assumed an uniform temperature throughout the cell. The model has been extended to include energy transfers, which enables the prediction of the interplay between the exothermic CO oxidation and the endothermic Boudouard reaction and the resulting temperature gradient in the fuel bed. The model also accounts for Joule heating throughout the electrolyte and considers conduction, convection, and radiation heat transfer.

![Diagram of the finite-element model](image)

**Figure 9:** The finite-element model accounts for heat transfer in the carbon bed (anode), the air and steam domains (cathode), and the electrolyte.

Our model is divided into modules that corresponds to the different compartments in our steam-carbon-air fuel cell (SCAFC), as seen in Fig. 9. The heat transfer treatment of this model is structured into the anode chamber containing the fuel bed, the cathode domains, and the electrolyte. The two cathode domains (steam and air) can be treated in a similar fashion as only the properties of the gases change between the two domains.

The heat transfer modeling in the solid fuel bed takes into account the effects of convection, conduction, and radiation through the following heat equation,

\[ \nabla \cdot (-k_{\text{eff}} \nabla T) + \rho_g C_p \bar{u} \cdot \nabla T = q_{\text{Boudouard}} \]  

Here, \( C_p \) is the heat capacity of the gas phase calculated by taking a weighted average of the heat capacities of pure gas phase constituents, which were computed using published NIST data.[57] \( q_{\text{Boudouard}} \) is the volumetric heat flux representing the energy required by the Boudouard reaction.

The first term of Eq. 1 requires determination of \( k_{\text{eff}} \), the effective thermal conductivity of a bed of particles containing stagnant gases in the void spaces. To do this, a relation originally put forth by Kunii and Smith [45] for the effective thermal
conduction of a bed of particles as a function of bed void fraction, solid and gas phase thermal conductivity, and particle emissivity is used. This relation takes into account various forms of conduction and radiation effects in the bed as summarized in Fig. 10. It has been validated against experimental data with particle diameters ranging from 27 µm to 8 mm and for a variety of particle types, [45] and is given by

$$k_{\text{eff}} = k_g \Psi_{\text{void}} + \frac{\beta(1-\Psi_{\text{void}})}{[\frac{k_g + D_p h_{r,s}}{\zeta} + \frac{\gamma}{k_s}]} + \beta h_{r,g} D_p \Psi_{\text{void}}$$

(2)

Figure 10: The effective thermal conductivity used in the energy equation for the anode bed (Eq. 2) accounts for: 1) Gas phase conduction, 2) Conduction between particles through stagnant fluid, 3) Conduction through solid particles, 4) Radiation between near-neighbor particles, 5) Radiation between distant particles.

Each of the terms in Eq. 2 must be specified in the model. The mean carbon particle diameter, $D_{ps}$, is taken as 155 µm [58] and the void fraction of the bed, $\Psi_{\text{void}}$, is estimated to be 0.4, [45] a value between the two limiting cases of 0.26 and 0.476 (found by considering different packing arrangements of hard spheres). The thermal conductivity of the gas mixture, $k_g$, is calculated using Chapman-Enskog theory of gases.[59] The solid thermal conductivity, $k_s$, was obtained from a relation published by Atkinson and Merrick [60] for coals, which depends on the density of the daf (dry ash free) material, $\rho_s$, and the temperature in kelvins to provide a value in W/(m-K),

$$k_s = \left(\frac{\rho_s}{4511}\right)^{3.5} \sqrt{T}$$

(3)

The parameters $\beta$ and $\gamma$ in Eq. [2] are geometric parameters for which Kunii and Smith recommend using a value of 0.9 and 0.67, respectively.[45] The value of $\zeta$, the ratio of effective thickness of stagnant fluid film around a particle to its diameter, depends on the void fraction of the bed and the ratio of the gas and solid thermal conductivities. Assuming a bed void fraction of 0.4 and a value for $k_s/k_g$ of 0.6, the value for $\zeta$ is determined to be 0.45 using the relations put forth by Kunii and Smith (omitted here in consideration of brevity). If the ratio of the gas and solid thermal conductivities is as high
as 10 or as low as 0.1, the value determined for \( k_{eff} \) changes by only 12% from its value when the ratio is 0.6, suggesting insignificant error in the effective thermal conductivity of the bed of particles due to uncertainties in the parameter \( \zeta \).

The remaining parameters in Eq. [2], \( h_{r,s} \) and \( h_{r,g} \), are radiative heat transfer coefficients. Yagi and Kunii [61] provide relations for both of these coefficients based on a particle bed model. Accordingly, the radiative heat transfer coefficient between neighboring solid particles in W/(m²·K) is given by,

\[
h_{r,s} = 0.2269 \, \frac{\varepsilon}{2-\varepsilon} \left( \frac{T}{100} \right)^3
\]

(4)

where \( T \) is the temperature in kelvins and \( \varepsilon \) is the emissivity of the particle. Values for emissivity of char particles depend on char type and devolatilization conditions and typically vary from 0.8 to 0.95. [61] Here a value of 0.85 is used, but any choice of emissivity within this range would only change the value of \( k_{eff} \) by at most 3%. For the radiative heat transfer between a particle and more distant particles via void spaces, Yagi and Kunii give

\[
h_{r,g} = 0.2269 \, \frac{1}{1 + \frac{\varepsilon}{2(1-\varepsilon)T}} \left( \frac{1}{T} \right)^3
\]

(5)

This coefficient also depends on the emissivity and temperature of the particle, as well as the void fraction of the bed.

In the cathode chambers of the cell, where a binary mixture of either \( \text{N}_2 \) and \( \text{O}_2 \) or \( \text{H}_2 \text{O} \) and \( \text{H}_2 \) is assumed, heat transfer via convection and conduction of the fluid are considered through the following conduction-convection equation,

\[
\nabla \cdot (\kappa \nabla T) + \rho c_p \bar{u} \cdot \nabla T = 0
\]

(6)

where the right-hand side is zero since there is no volumetric heat source term in the cathode domains.

The electrolyte is not modeled in the finite element model, but is instead treated as a 1-D finite slab that ties the anode and cathode compartments together through boundary conditions. In the electrolyte, the heat transfer phenomenon of significance is Joule heating due to finite resistance to ion transport and conduction due to the temperature difference between the anode and cathode surfaces. In addition, there are enthalpy considerations due to the half-cell reactions occurring on the electrode surfaces. In this model, the two electrode reactions for each membrane are lumped together and placed on the anode surface due to lack of thermodynamic data for ionic species. Due to the low conductive resistance between the two electrode surfaces, this approximation has no significant effect on the model results. The inward surface flux into the anode compartment is hence

\[
q_{YSZ,a} = k_{YSZ} \frac{T_c - T_a}{t_{YSZ}} + \frac{j^2 t_{YSZ}}{2 \sigma_{YSZ}} + \left( \frac{1}{2F} \right) \Delta h_{rxn}
\]

(7)

Here \( t_{YSZ} \) is the electrolyte thickness, and \( k_{YSZ} \) is the thermal conductivity of the electrolyte taken to be 2 W/m*K, which was found to be a valid estimate for the entire temperature range of interest. [62] The first term on the right hand side of Eq. [7]
represents conduction through the YSZ electrolyte, the second term Joule heating, and the third term, the combined enthalpy increase due to the two half-cell reactions for the membrane in question. It is found that the heat release due to the overall fuel cell reaction is significantly more important than the heat release due to Joule heating for all achievable current densities. Only at very high current densities does Joule heating start to have an impact, but the term is included here for completeness. For example, for the air-carbon cell at 1 A/cm$^2$ and 900 °C, the heat release due to Joule heating is only one eighth of the heat release due to the overall fuel cell reaction.

On the cathode side, the inward surface flux is similarly given by

$$q_{YSZ,c} = k_{YSZ} \frac{T_a - T_c}{\Delta T_{YSZ}} + \frac{j^2 \sigma_{YSZ}}{2}$$

The energy equations presented in the preceding paragraphs are not specific to a particular geometry or system, and can be applied to a specific case by suitable application of boundary conditions. In Fig. 11, the temperature distribution in the fuel bed of a planar air-carbon cell is investigated and plotted for several different fuel bed heights. The cell is kept at a representative voltage of 0.7 V and the cathode electrode surface is kept at 1173 K. The temperature distribution in the fuel bed is important since higher temperatures promote faster reaction kinetics.

![Figure 11: Temperature in the fuel bed as a function of distance from the anode surface for bed heights of 4, 8, 12, 16, and 20 mm, at a cell operating voltage of 0.7 V.](image)

The temperature drops with increased distance from the anode surface due to limited heat transfer through the fuel bed, as well as the endothermic Boudouard reaction in the bed. As carbon monoxide production from gasification decreases exponentially with temperature, even a modest decrease in bed temperature renders bed regions slightly away from the anode surface comparatively less active. Having a less active bed requires a higher bed of carbon in order to maintain a prescribed power output of the cell. Clearly,
a bed height higher than necessary is not desirable and high conversion efficiencies require small bed heights. Ideally, one would have a highly active bed in close proximity to the anode surface such that the likelihood for CO diffusion back toward the anode surface instead of leaving the system in the exhaust is maximized. A highly active bed can be achieved by choosing a chemically active fuel with a high number of reaction sites. Furthermore, effective thermal management of the carbon fuel cell would promote an uniform temperature distribution throughout the fuel bed and hence a higher performance.

The overall thermal requirements of the air-carbon cell as a function of cell voltage and height of the fuel bed were also investigated. Typical results are shown in Fig. 12. The model was run for voltages ranging from short circuit to cell OCV and for fuel bed heights ranging from 1 to 8 mm.

![Figure 12](image)

**Figure 12:** Model results showing the thermal requirements of the planar air-carbon cell. Heat requirements are plotted as a function of fuel bed height and cell voltage. Endothermic and exothermic regions are identified, as well as the contour for autothermal operation of the cell.

The results shown in Fig. 12 shows the interplay between the endothermic Boudouard reaction and the overall exothermic half-cell reaction at the anode surface. The cell operates in a mildly endothermic manner at high cell voltages for all fuel bed heights, and exothermically for most voltages below approximately 0.8 V. It is clear from Fig. 12 that the cell can be run at autothermal mode at around 0.8 V, which is a desirably high cell voltage for practical reasons. Most fuel cells operate at voltages considerably below this value, which necessitates more cells to be connected in series in order to build up the voltage output of the unit. At very low voltages, the cell becomes significantly more exothermic, rejecting large quantities of waste heat. In between, at the autothermal
contour, the cell neither requires energy input to maintain operation nor rejects any energy as waste heat. Operation of the cell is preferred in either an autothermal or mildly exothermic region in order to maximize efficiency. In all cases, thermal contours seem to be practically insensitive to the height of the solid bed within the regime of interest. Note that the results shown in Fig. 12 indicate the thermal requirements for the air-carbon cell only. The steam-carbon cell is by itself endothermic and consequently, an integration of the two cells, which is the proposed scheme in this project, is desirable. A heat transfer analysis of the coupled steam-carbon-air fuel cell is underway.

Progress

This project promises to contribute significantly to mitigating CO₂ emissions from coal power generation in two major ways, namely, a) dramatic improvements in conversion efficiencies naturally translate into proportionately less emissions, and b) a process flue gas stream consisting primarily of CO₂ eliminates the necessity for costly post-separation processes from nitrogen.

This fuel cell scheme is also distinctly different from conventional steam reforming of hydrocarbons and various coal and biomass gasification processes for producing hydrogen, where the hydrogen is derived from both the steam and the hydrocarbon or the coal or biomass fuel used for gasification. By contrast, in this project, the hydrogen is supplied solely from water (i.e., steam), not by coal or biomass. In addition, unlike steam reforming and gasification processes, which require energy intensive separation steps to remove COₓ gases down to trace quantities from hydrogen, the two product streams in this project do not mix at all and are physically separated at all times by the impervious ceramic membrane. The resulting cathode product gas is pure H₂ with unreacted steam, but no contamination from COₓ gases. Steam can easily be condensed to produce a high-purity hydrogen product stream for use as an energy carrier for large scale storage or an effective fuel for polymer exchange membrane fuel cells (PEMFC) for transportation applications. Carbon-free purity in hydrogen is a critical consideration for near-room temperature hydrogen fuel cell applications, where even trace levels of CO in the H₂ fuel feed may be detrimental to the operation and long term performance of the fuel cell due to catalyst deactivation.

Another advantage offered by this project is that carbon dioxide is used for gasifying the coal bed instead of steam, which is otherwise used typically in all coal gasification applications. Use of CO₂ minimizes the coking problems that have hindered previous attempts to immerse solid oxide fuel cells in steam gasified carbon beds.

This project provides a significant innovation towards total independence of the steam electrolysis process from the electricity grid by thermally and physically coupling a steam-carbon fuel cell directly with an air-carbon fuel cell, such that the two cells share the same coal/biomass bed as the anode compartment while the corresponding cathode compartments contain steam and air, respectively. The coupled fuel cell arrangement allows simultaneous and spontaneous production of electrical power and/or carbon-free hydrogen, such that the production rates of each can be adjusted at will based on the relative demands for power generation or chemical storage. In addition to such flexibility, this scheme offers several important advantages, namely, 1) efficient generation of power during peak demand times for load leveling, 2) large-scale chemical storage of electrical energy at off-peak times in hydrogen which is an effective and clean energy carrier, 3)
reduced emissions of CO₂ into the environment, 4) production of highly concentrated CO₂ (> 90%) in the flue gas that eliminates the need for separation from nitrogen, and 5) distributed generation of power and hydrogen from local resources such as biomass.

During the past year, substantial efforts have been put into upgrading the experimental facilities in lab and hiring qualified researchers to work on the project. Additionally, Michael Stewart who earned his PhD in Chemistry in December 2013 has joined our research group (in January 2014) and brings in a wealth of expertise in materials synthesis and catalysis with hands-on experience with fuel cells. Also, first year chemical engineering graduate student Brandon Loong has just joined our group in April 2014, expanding our personnel and expertise base as well as providing additional skills.

The new instrumentations acquired include three potentiostats from Gamry with different current compliance capabilities and a gas chromatograph (GC) from Bruker. The potentiostats enable a variety of electrochemical measurements including potentiostatic, cyclic voltammetry, and electrochemical impedance measurements. The GC includes a dual thermal conductivity detector (TCD) for H₂, CO, CO₂, CH₄, and other permanent gas measurements and a pulsed flame photometric detector (PFPD) for measurement of sulfur containing species formed during coal oxidation. The experimental capabilities have been expanded from one fuel test stand to three operating test stands. One of these test stands will be dedicated to proof-of-concept and system demonstrations, while the other two will be dedicated to catalytic studies of sulfur-tolerant anodes and improved cathode materials for steam reduction. A micro-reactor test fixture for sulfur sorbents studies, which will be self-contained in chemical fume hood for safety reasons is under construction. With new instrumentation, improved experimental facilities, and sufficient personnel to conduct experiments, high productivity and scientific progress is expected over the upcoming months.

While only preliminary results are shown here, within the next year we expect to have screened all known sulfur tolerant anode materials, water splitting catalysts, sulfur sorbents, as well as have developed new and better materials of our own. Moreover, with our current facilities we will be able to move towards building and running a prototype device for hydrogen production.

Future Plans

During the next twelve months, we will down-select materials for sulfur tolerant anodes. However, this will be done in parallel with the development and testing of catalysts for water splitting, so that screening of both sulfur tolerant anode materials and hydrogen splitting catalysts can be finished before the next annual report. With both sulfur tolerant anode materials and water splitting cathode materials identified, it will be possible to build a working prototype fuel cell for the proposed scheme.

Moreover, parallel work will be carried out for identifying and screening promising sulfur sorbents. Naturally, this selection process will involve both experimental studies and thermodynamic predictions. In terms of experiments, the next step in characterizing these materials for the carbon-steam fuel cell is to evaluate their performance under sulfur-free and 10 ppm H₂S/10 % CO conditions. As mentioned earlier, test stands for screening of these materials have been built, and we are currently assembling membrane electrode assemblies for characterization.
Unlike work done by other groups characterizing fuel cells, we will also be incorporating a reference electrode to more accurately measure local potential and current at each electrode, and obtain better insight into the dominant electrode rate processes. As shown schematically in Fig. 13, we will use masks to selectively screen print electrodes onto electrolyte wafers. On heating, both the pore formers and mask will be burned off leaving only the template electrode layer. By leaving a small, electrode free region in the center of the anode electrode, it will be possible to attach a gold or silver reference electrode. As the reference electrode is in the center of the electrode layer, there will be no flow field effects on the measurement.

**Figure 13:** Schematic for assembling MEAs with reference electrodes; grey boxes represent silver current collectors, the top set that are separated by a mica spacer. The reference electrode is connected to the electrode of interest.

Additionally, char reactivity studies are planned concurrently with materials selection tasks as well as testing the viability of various biomass sources as fuels, such as almond shells, coconut husks, and corn stover. Due to the low sulfur content of biomass sources, it is possible to screen biomass materials with a standard Ni/YSZ anode while simultaneously developing better anode materials.

Finally, improving the system model beyond the preliminary stage to include reactions on the MEA will be developed and implement. A breakdown of the individual project tasks are summarized below in Table III.
As shown in Table III, parallel efforts were anticipated with fuel cell characterization and anode development studies (Tasks 1, 2 and 3) proceeding at nearly the same time as the sorbent, char conversion and system modeling studies (Tasks 4, 5, and 7), activities in both groups starting at the beginning of the project. The framework for advanced modeling of the coupled fuel cell would begin in the second year of the project, with the model being updated as results from the other tasks become available. Currently Tasks 2, 4, and 7 are underway, and Tasks 3 and 5 will begin within the next few months. We expect by the end of the year that Tasks 2, 4, and 5 will be completed, and Tasks 1, 3, and 6 will be started.

**Publications**


Note: This publication was not supported by GCEP but was conducted as a preliminary study in anticipation of a possible GCEP award.

**Conference Presentations:**

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