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IICEC ENERGY AND CLIMATE RESEARCH PAPER

Using Natural Gas as an Environmentally Sustainable Power Source with Solid Oxide Fuel Cells

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1. Summary

Policies, research and pilot projects to commercialize carbon capture in the power sector have focused on coal plants. However, the expected world-wide consumption of natural gas in the power sector is not consistent with a sustainable environmental future without also employing carbon capture technologies to natural gas plants. One reason carbon capture from natural gas has not received much attention is, as will be discussed below, the very high cost of carbon capture from natural gas plants compared to the already considerable cost of carbon capture from coal plants. Capture of carbon with conventional natural gas turbines is not economically practical. Consequently, a different technology is needed to generate electricity from natural gas in the power sector. This technology should be competitive with natural gas turbines (disregarding its ability to employ carbon capture). This technology should permit the capture of carbon at low cost. Ideally, the cost should be significantly lower than the cost of carbon capture from coal plants (as measured by the cost per ton of captured CO₂).

Solid oxide fuel cells (SOFCs) are the leading technology to meet these requirements. Their emissions of CO₂ without carbon capture are relatively low due to their high efficiency. Significantly, in the SOFC exhaust, CO₂ is only comingled with water and unreacted CH₄. This enables low-cost separation of CO₂. In addition, the efficiency losses from the application of carbon capture are minimal compared to the significant efficiency losses when carbon capture is applied to coal power plants or natural gas turbines.

The primary barrier to the uptake of SOFCs is the development of a grid-scale SOFC with a comparable cost and reliability compared to the natural gas turbine. With a cost-competitive grid scale SOFC technology, the additional cost of carbon capture would be minimal compared to the cost-prohibitive carbon capture technologies that are available for coal power plants and natural gas turbines. Consequently, commercialization of carbon capture in the power sector could be achieved with policies that impose a *much* lower burden on the economy and a *much* lower increase of the cost of electricity than is now the case.

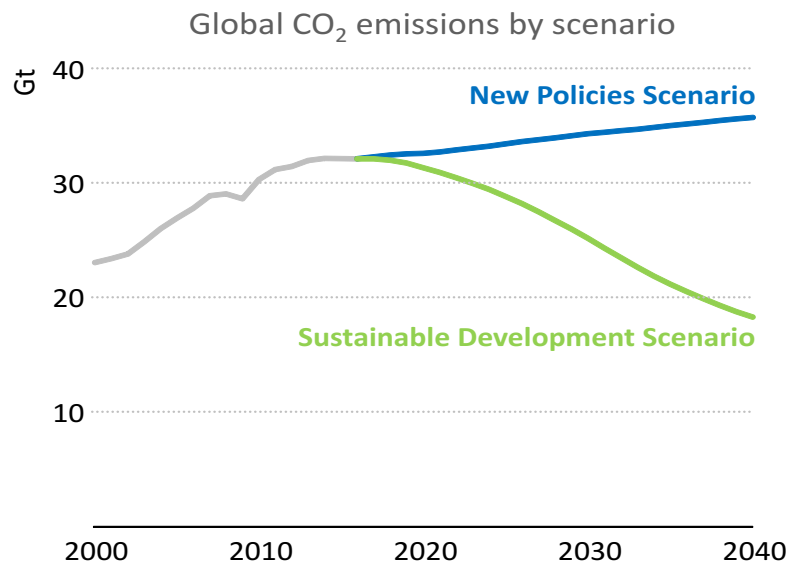
While the current research to achieve cost-competitive and reliable SOFCs for grid-scale application is encouraging, these efforts should be significantly increased in order to achieve more rapid technology development and the opportunity to achieve grid-scale commercial application, a necessary step that enables further cost reduction (technology learning, or, learning by doing).

2. Introduction

There is a critical need to provide electric services for a growing worldwide population that is experiencing rapid economic development in some of the most populous countries. At the same time, these services must be provided with dramatically lower greenhouse gas (GHG) emissions. Multiple studies have shown that the power-sector would have to achieve deep cuts in GHG emissions in order to make significant cuts in overall GHG emissions. This is because a large share of energy-sector GHG emissions come from the power sector and reducing GHG emissions in the power sector

is relatively cost effective compared to reducing emissions in other sectors (especially the transportation sector).ⁱ Consequently, it is important to increase efforts to use electricity efficiently and provide electricity from near-zero greenhouse gas sources. However, fossil fuels such as coal, oil and natural gas have been widely used to generate electricity over the last two hundred years and, along with the use of fossil fuels in other sectors of the economy, is responsible for higher GHG concentrations in the atmosphere and a consequent global warming trend. Notwithstanding political measures, consumer trends, market dynamics and societal awareness to address the climate-change problem, all efforts to reduce energy-sector GHG emissions are expected to fall short of meeting the 2°C target established by the United Nations.ⁱⁱ It is difficult for governments to take dramatic actions to limit GHG emissions if those actions limit or significantly increase the cost of energy, especially in the developing world. In order to commercialize low-GHG technologies, such as renewable energy and using fossil fuels with carbon capture and storage, these technologies must be capable of providing energy services at a reasonable cost and, preferably, providing energy services at the lowest cost. The challenge is formidable as shown in Figure 1.

Figure 1: International Energy Agency CO₂ Emission Scenariosⁱⁱⁱ



Based on analysis recently completed for the International Energy Agency’s *2017 World Energy Outlook*,^{iv} the policies that were likely to be adopted by countries absent compliance with the Paris Accord are estimated to produce steadily growing CO₂ to over 35 GT/y through 2040. In contrast, the sustainable development scenario, in line with the objectives of the Paris Accord, required that CO₂ emissions decrease steadily to less than 20 GT/y by 2040. As noted above, the power sector must play a key role in bringing about reduced CO₂ emissions.

The power sector is also important for reducing emissions from the transport sector as government policies and the motor vehicle industry turn to plug-in electric vehicles (PEVs) as a way of reducing light-duty vehicle CO₂ emissions. Without significant CO₂ emissions reductions in the power sector, the PEV strategy would fall well short of its expected GHG-reduction benefit. While renewable

energy is growing rapidly to help meet this challenge (from 2000 to 2016, more GW capacity of renewable power was added than all other sources combined^v), however, there may be limits to what renewable energy can accomplish by itself.^{vi} Other low-GHG emission technologies may be needed. Nuclear power has long held promise to provide competitive baseload power with very low GHG emissions. However, recent experience has shown that high cost and huge financial risks make it much less likely that new nuclear reactors will be built in competitive power markets without government support.^{vii} Government support is available in several countries in Eastern Europe, the Middle East and Asia where nuclear power investments are proceeding. However, nuclear capacity additions (12 GW/yr) are expected to lag far behind renewables (208 GW/yr), natural gas (71 GW/yr) and coal (40 GW/yr) through 2040.^{viii} Continued capacity additions for natural gas and coal power plants reflect the ample world-wide supplies of natural gas and coal. The more rapid growth of natural gas in the power sector, compared to coal, can also be explained by its environmental benefits. Nevertheless, these additional natural gas plants, not to mention the additional coal plants, will not be compatible with a sustainable emissions trajectory without the addition of carbon capture and storage technologies. It should also be noted that, while natural gas power plants have about half of the CO₂ emissions per kWh than coal, since the estimated capacity additions for natural gas are almost double those for coal, removing CO₂ from natural gas plants is no less urgent.

3. Overview of Carbon Capture and Storage

Carbon Capture and Storage (CCS) removes CO₂ from a fossil-fuel-using energy source (such as a coal- or natural gas-powered power plant) and transports it via pipeline to be pumped deep enough into the earth to secure safe, long-term storage.² Storage reservoirs include deep saline formations, depleted oil and gas wells, and unminable coal beds. These reservoirs have cap-rock that would prevent CO₂ from migrating to the surface.

CCS could be one of the most important methods to reduce of CO₂ emissions. Depending on the world's continued reliance on fossil fuels, CCS has the potential to be of comparable importance to energy efficiency, renewable energy or nuclear power. However, CCS is a relatively undeveloped technology, at least for the purpose of reducing CO₂ emissions, as CO₂ injection is typically used for tertiary oil recovery.³ The earliest application of CCS for the purpose of avoiding CO₂ emissions was the Weyburn-Midale Carbon Dioxide Project (2002). The CO₂ injected into the Weyburn-Midale fields was derived from a coal-gasification power plant. While the Weyburn-Midale and some other CCS demonstration projects have provided valuable data on the cost and feasibility of CCS, CCS has failed to emerge as a commercial-scale method to reduce of CO₂ emissions.

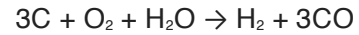
² Carbon capture utilization and storage (CCUS) also includes the use of CO₂ captured from power plants for enhanced oil recovery or other industrial or commercial uses. While an important stepping stone for CO₂ capture, since CO₂ would have a value stream if used, the volume of CO₂ that must be removed to achieve sustainable use of fossil fuels far exceeds the industrial or commercial needs for CO₂. Consequently, the above discussion focuses on CO₂ storage but we use the acronym "CCS" to also include utilization projects.

³ However, in almost all cases, the use of CO₂ for tertiary oil recovery does not employ CO₂ that was derived from man-made sources. Consequently, the CO₂ is merely moved from one underground reservoir to another.

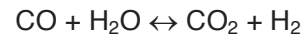
4. Carbon Capture from Coal

The primary barrier to the uptake of CCS has been the high cost of CO₂ separation during the process of burning fossil fuels to produce electric power. Various methods have been developed but can be classified into three types: 1) pre-combustion, 2) oxy-combustion; and 3) post-combustion. The technology used in the pre-combustion approach uses coal-gasification and water shift reaction to produce CO₂ and H₂ (see the adjacent box for more detail). The H₂ is provided to a turbine and the CO₂ is compressed for transport and storage. In essence, a chemical plant and hydrogen-fired turbine *replaces* the conventional coal power plant where coal is burnt to produce steam for steam turbines. The cost per kWh of a pre-combustion CCS plant would be at least 32% higher than a standard coal plant that meets strict environmental requirements.^{ix}

Coal is partially oxidized in a gasifier producing CO and H₂ (syngas).



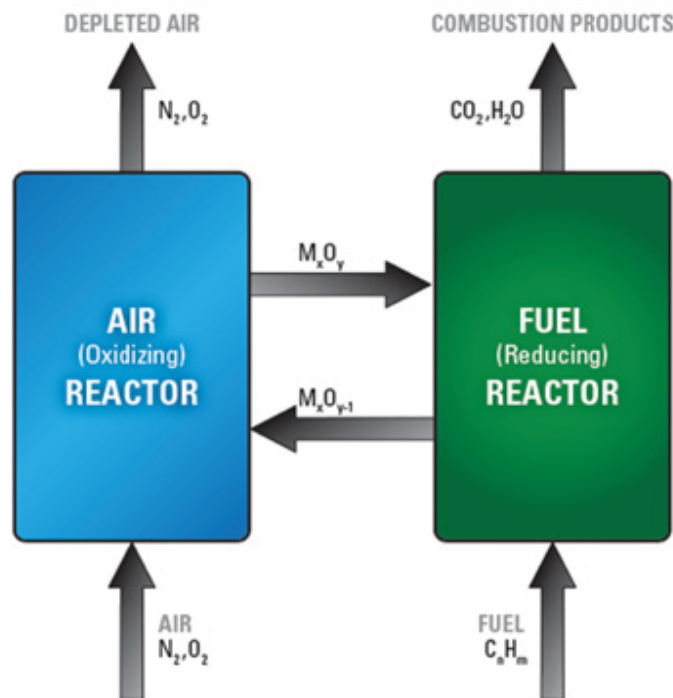
For precombustion CCS, more hydrogen is gained with a water shift reaction and, more significantly, the CO reacts to become CO₂.



The H₂ is sent to a turbine to produce electricity while the CO₂ is compressed to transport via pipeline for sequestration.

Oxy-combustion can be employed to produce a flue gas that is almost entirely CO₂ which then can be compressed and stored. By combusting coal with oxygen, one avoids having to separate CO₂ from the flue gas that contains a considerable volume of air as well as NO_x. The main problem with this approach is the expense (45% more expensive per kWh) and the high energy consumption of separating CO₂ from air. A promising alternative to air

Figure 2: Chemical Looping^x



separation is chemical looping in which a metal oxide is used to provide oxygen to a fluidized bed for coal combustion. The oxygen-depleted metal oxide is “looped back” to recapture oxygen and

again return oxygen to the fluidized bed. Figure 2 (above) illustrates this process. The “fuel reactor” is the fluidized bed of the steam coal plant receiving its oxygen from the “air reactor” in the form of a metal oxide, absent any N₂. The oxygen-depleted metal oxide returns to the air reactor where oxygen is recovered and it circulates again to the fuel reactor to provide more oxygen for coal combustion. This process avoids the high energy consumption of air separation and could offer a relatively cost-effective approach to achieve carbon capture from coal. However, while promising research is being conducted on this method, there is, as yet, no commercial application of the technology.

Post-combustion capture of CO₂ typically uses techniques such as carbon scrubbing or membrane gas separation. Since the percentage of CO₂ and pressure in the flue gas is relatively low, post-combustion capture cannot be expected to remove as high a percentage of CO₂ as pre-combustion or oxy-fuel technologies. Post-combustion capture is estimated to increase the cost of power from coal power plants by 32% to 70%.^{xi, xii} As with pre-combustion removal of CO₂, commercially available carbon capture technologies would raise the cost of coal power plants to un-economic levels as well as making them less efficient.

The estimated costs of CO₂ capture from coal are presented in Table 2 (on pg.8). They range from \$35 to \$45 per ton of CO₂. These costs are not outside the bounds of future carbon-costing regimes. Nonetheless, they do not fully reflect the costly and difficult pathway needed to achieve commercial scale CCS from coal. The time required to transform subsidized pilot projects to scalable and economically viable plants, at these carbon prices, is likely to take decades. The IEA *Energy Technology Perspectives* reports provide “pathways” to CCS commercialization but actual progress versus estimated requirements regularly fall short. According to Nykvist, international funding for carbon capture from coal would have to increase by a factor of 10 in order to achieve the IEA CCS scenarios.^{xiii}

5. The Natural Gas Revolution

In years past, there has been little discussion of using carbon capture and storage for natural gas plants. There were two main reasons for this. First, coal seemed to be a more natural target since a coal plant has twice the carbon emissions per kWh of electricity produced than a natural gas plant.^{xiv} Second, natural gas was not perceived to be a fuel that would be available in abundant quantities, at competitive prices, far enough into the future to expect the long-term use of natural gas in the power sector. Capital investments in natural gas plants are recovered quickly insulating investors from the risks of longer term increases in the price of natural gas. Natural gas supplies were dominated by Russia and the Middle East and there were not any expectations that a transparent global market for natural gas would ever evolve.

The picture today is very different. Vast reserves of tight gas have now become economically recoverable. Using the technologies of horizontal drilling and hydraulic fracturing, many tight gas formations can yield large quantities of natural gas at low cost. Consequently, as shown in Table 1 (below), economically recoverable natural gas reserves are now estimated to be large enough to fuel the world’s power sector for many decades. In addition, as shown in Figure 3, the currently estimated

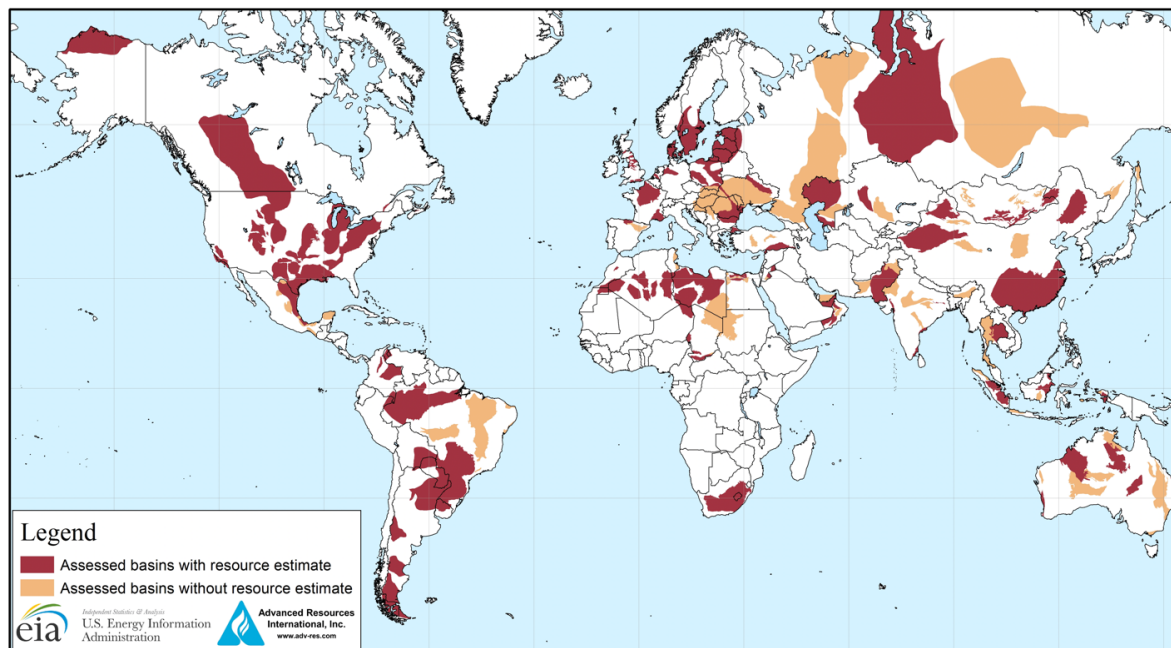
unproven economically recoverable shale gas reserves of over 337 trillion cubic meters are more evenly distributed among world regions than conventional natural gas reserves.

Table 1: Economically Recoverable Natural Gas Reserves by Region^{xv}

Region	Conventional	Unconventional
Eastern Europe & Eurasia	160	43
Middle East	132	12
Asia Pacific	44	93
OECD Americas	81	82
Latin America (non-OECD)	27	48
Africa	35	22
OECD Europe	35	22
World Total	519	337

Figure 3^{xvi} also highlights the fact that unconventional gas reserves are often located near population centers, making the transport of produced natural gas more economic.

Figure 3: World-Wide Distribution of Unconventional Natural Gas Reserves



The impact on new economically recoverable reserves of natural gas is also evident in the recent projections of natural gas production. By 2040, the IEA projects that annual natural gas production from unconventional resources will increase by 1,061 billion cubic meters while increasing by only 622 billion cubic meters from conventional sources. Overall natural gas production is expected to increase from 3,536 billion cubic meters to 5,219 billion cubic meters.^{xvii}

With public policies and considering the cost of CCS technologies for coal plants, coal is expected to be in significant decline in order to meet the emission targets necessary to limit greenhouse gas concentrations to 450 parts per million. The IEA expects, in the “2 Degree Scenario,” that the production of electricity from coal will only be one-quarter as much in 2040 than it was in 2014.^{xviii} While natural gas plants have relatively low carbon emissions compared to coal, they are still too high to be compatible with the 2 Degree scenario. Keeping natural gas fired power plants in a 2 Degree future will require CO₂ capture and storage.

6. Carbon Capture from Natural Gas

In emission reduction regimes driven by the “cost of carbon” approach, the use of carbon capture from natural gas is more challenging than it would be for coal. In these carbon markets, the most cost-effective carbon reduction technologies are employed before others. Consequently, if there was a price on carbon, the priority would be to use carbon capture for coal plants well before it would be used for natural gas plants. For example, the technologies for post combustion separation of CO₂ from coal and natural gas are similar except that the cost per ton of CO₂ removed from natural gas would be much higher because the concentration of CO₂ in the flue gas is much lower.

The worst approach for removal of CO₂ from natural gas, relative to the equivalent methods that could be applied to coal, is pre-combustion separation. Unlike the integrated gasification combined cycle (IGCC) approach used for coal, the steam reforming and water shift units do not *replace* anything. For coal, with the addition of the coal gasification unit and hydrogen-powered turbines, this hardware *replaces* the steam coal plant. For natural gas, the hardware to convert CH₄ to CO₂ and H₂ is an *additional* cost since the plant still requires combustion turbines to produce electricity (in addition, the turbines are likely to be more expensive since the natural gas turbines must be replaced by turbines that can tolerate a much higher percentage of hydrogen with consequently higher combustion temperatures). Oxy-fuel combustion is also much more expensive for a natural gas plant as cryogenic distillation technology that could be employed and would also require a redesigned natural gas turbine.^{xix}

The estimated costs of CO₂ separation in coal and natural gas plants are summarized in Table 2.

Table 2: Cost Comparison of CO₂ Separation: Coal vs. Natural Gas^{xx}
(2018USD)

Type of Power Plant	Pre-Combustion	Oxy-Fuel	Post-Combustion
Pulverized Coal	\$29/ton CO ₂	\$45/ton CO ₂	\$42/ton CO ₂
Natural Gas Combined Cycle	\$139/ton CO ₂	\$126/ton CO ₂	\$72/ton CO ₂

Note: Costs include CO₂ compression to 110 bar, excluding storage and transportation costs.

As discussed above, using pre-combustion for natural gas is quite expensive, \$139/ton of CO₂, because there is no offsetting savings achieved by *replacing* the pulverized coal plant with an IGCC plant. Pre-combustion capture simply *adds* chemical processing while still relying on combustion turbines to produce electricity. Oxy-fuel combustion is estimated to be slightly less expensive per

ton of CO₂ than precombustion removal but this cost does not include the likely higher cost of the redesigned natural gas turbine. The costs of CO₂ separation from the flue gas are estimated to be about twice as high for a natural gas plant compared to a coal plant, reflecting the lower amount of CO₂ saved per kWh of electricity produced.

If natural gas is to remain a viable long-term power-sector fuel in a “2-Degree” world, there will have to be a more cost-effective way to capture CO₂ from a natural gas plant than the technologies reviewed above. Ideally, this gas-to-electricity generation technology should be competitive with natural gas turbines and also capture CO₂ emissions with minimal additional cost. In addition, the technology, unlike the current CCS concepts that could be used for coal or natural gas, should not require complex pilot projects that would take several years or decades before becoming commercially scalable power plants. A promising technology that may be able to meet these requirements is the solid-oxide fuel cell (SOFC) and it is the *raison d’etre* for this paper.

7. Current Deployment of Solid Oxide Fuel Cells in the Power Sector

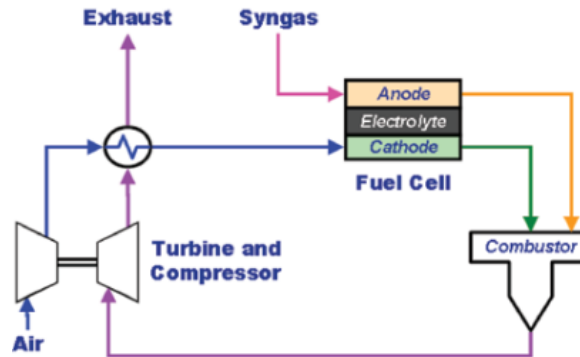
SOFCs are a commercially produced product for niche markets. For example, Bloom Energy markets power from their SOFCs (up to 250 kW capacity) to power the headquarters of several large California companies (a U.S. State with relatively high electricity prices).^{xxi} In Germany, Bosch Thermotechnology markets its SOFCs to provide decentralised power and heat services in residential applications. Bosch emphasizes its high efficiency compared to other decentralised power and heat generators claiming a 50% reduction of CO₂ emissions “compared to conventional power and heat generation.”^{xxii} Other companies offering SOFCs for residential and other distributed power applications are Convion (Finland),^{xxiii} Elcogen (Finland/Estonia),^{xxiv} and CERES Power (UK), although there are several others supplying this market.

Larger SOFCs are marketed by Mitsubishi and other companies. Mitsubishi offers a 1,000kW hybrid unit (described below) for industrial applications.^{xxv} As discussed below, the efficiency of an advanced hybrid system could potentially increase to over 70%. An important factor behind the recent commercial interest in marketing SOFCs is the significant potential that exists for cost reduction using thin ceramic electrolytes and lower operating temperatures, as well as other design features to increase efficiency (some of the products mentioned above incorporate these technologies).^{xxvi} While SOFCs cannot now compete with natural gas turbines as a reliable cost-effective grid scale technology for utilities or independent power producers, there is a significant likelihood that government and academic research, along with commercial development, will produce a competitive grid-scale SOFC industry.

8. Solid Oxide Fuel Cells Explained⁴

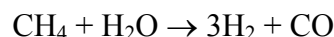
Owing to their high operating temperature, high efficiency and fuel flexibility,^{xxvii} SOFCs are the most suitable candidate for hybridization with combustion based thermal power systems. The most typical configuration is the integration of the SOFC with a gas turbine.^{xxviii} Figure 4 shows a diagram of a typical SOFC – gas turbine hybrid system.

Figure 4: SOFC-Gas Turbine Hybrid System^{xxix}



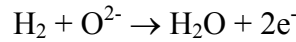
Typical cycle includes a compressor, a gas turbine, a combustor and the SOFC. Without the fuel cell, the heat engine is a Brayton cycle, where the high pressure compressed air enters into a combustor where the energy from the fossil fuel increases its energy, which is converted into useful work in the turbine. While a part of the work from the turbine is used in the compressor, the rest is converted into electricity. The fuel cell is placed before the combustor and converts the part of the energy in the syngas (which is the mixture of partially reformed hydro-carbon, such as natural gas, hydrogen and carbon monoxide) into electricity directly with high efficiency 60% or more. The exhaust of the fuel cell is rich with fuel and unburned hydrogen, carbon-dioxide and water vapor. The remaining fuel in the exhaust can be burned directly with oxygen (much less than the total oxygen required to burn the hydro-carbon, as most of it, about 80%, has already been converted into CO₂ and H₂O) to produce more carbon-dioxide and water vapor. The exhaust that exits the turbine is the mixture of CO₂ and H₂O, which can be condensed and CO₂ can be removed. Alternatively, CO₂ can be removed from the fuel cell exhaust and the combustion of the remaining fuel with air, and in this way, it still achieves (not perfect but) a very high CO₂ capture as well in the overall.

Typical SOFC arrangement consists of ceramic-based porous anode and cathode electrodes and a solid electrolyte as shown in Figure 5. When hydrocarbons are used as fuel, reforming reaction of hydrocarbons with water vapor produces carbon monoxide and hydrogen in the anode. For example, methane reforms to hydrogen and carbon-monoxide:

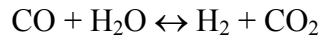
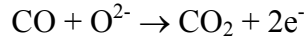


⁴ An overview of other fuel cell technologies is provided in Appendix 1.

Electrochemical reaction of hydrogen with oxygen ions coming from the cathode is the main reaction in the anode as water being the only product in addition to electrons that make up the current that flows in the circuit:

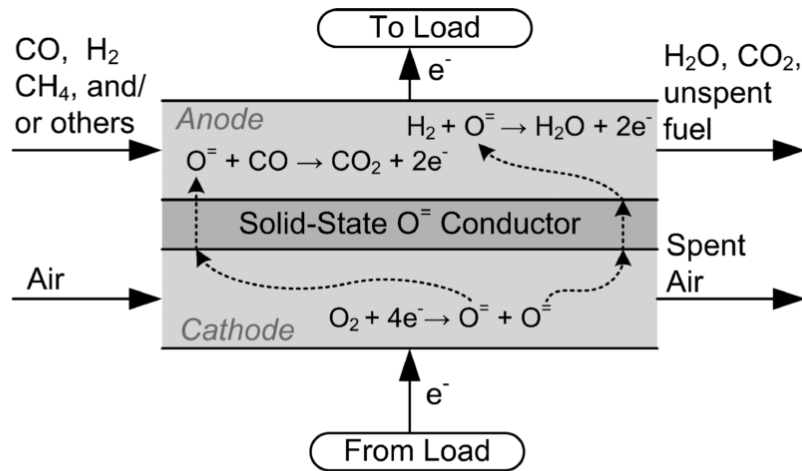


Carbon monoxide from the main reforming reaction can react with oxygen ions to form carbon dioxide directly, or in the presence of sufficient water vapor, water-gas-shift reaction generates hydrogen and carbon dioxide as well:



Overall, fuel enters to the anode and water vapor and carbon dioxide exit as products along with unspent fuel if fuel-rich operation is preferred. In fact, extra fuel in the anode side is always desirable to ensure uniform current and reactions throughout the cell as starvation of fuel is often associated with undesirable degradation issues. The cathode operates with air, as atmospheric air enters and oxygen-depleted air exits.

Figure 5: Layout of SOFC Operation^{xxx}



The main role of the electrolyte is to keep the reactant gases in the anode and the cathode separate and allow only oxygen ions to transfer from the cathode to the anode. Whereas porous electrodes ensure diffusion of gas species to reaction sites and conduct electrons. SOFC electrolyte is made of a solid material, such as yttria-stabilized zirconia (YSZ), which is a good ionic conductor at high temperatures (600 – 1000 °C) but acts as a barrier for gaseous reactants.^{xxxi} In addition to YSZ, a number of ionic conductors have been studied to attain improved ionic conductivity at lower temperatures, such as gadolinia or samaria-based ceria (GDC or SDC). YSZ is also used in the anode electrode as a part of the porous ceramic-metallic (cermet) composite, which contains nickel as a common metal because of its favorable electric properties and as a catalyst that promotes the oxidation of the fuel and the reforming reaction. SOFC cathodes are made of porous oxides having a stable

perovskite structure with good electric properties at high temperatures in an oxygen rich environment. Most widely used cathode materials are strontium-doped lanthanum manganite (LSM), cobaltite (LSC), ferrite (LSF) and cobalt ferrite (LSCF). Despite excellent electronic and ionic conduction properties and stability in oxidizing environments, cathode materials are not suitable in the anode due to reduction by the fuel.^{xxxii}

There are two basic SOFC geometries: planar and tubular.^{xxxiii} In the planar geometry electrolyte is sandwiched between the electrodes in individual planar cells, which are placed side-by-side to form an SOFC stack. The main advantage of the planar structure is the current collection in series, and simplicity of the manufacturing process. However, the distribution of the fuel flow in the anode and the air flow in the cathode requires attention. Similarly, thermal stresses during transients can become major issues in the lifetime and the durability of the stack.

In the tubular design, the stack is formed by parallel construction of cylindrical tubes having the anodes inside and the cathodes outside and manufactured by ceramic extrusion process. Tubes are supported by a relatively thicker (*ca.* 200 μm) anode material, which is a mix of a ceramic material, typically YSZ with nickel, which serves as an electric conductor as well as a catalyst. The anode support is wrapped by thin shells (*ca.* 30-40 μm) of electrolyte and the cathode can be made very thin to improve the overall performance, efficiency and the power density of the cell. Flow distribution in the tubular designs is less of an issue than the planar ones as the tubes open to inlet and outlet manifolds that enable even distribution of reactants inside and outside the tubes. In addition, tubular designs are less prone to thermal stresses than the planar ones. However, the current collection requires elaborate wiring with high temperature resilient alloys such as Crofer 22 APU^{xxxiv} inside and outside the tubes. In the tubular design, further improvements to power density and performance can be achieved as the diameter of the tube decreases. In micro-tubular SOFCs, the tube diameter can be smaller than 1 millimeter and up to a few millimeters. These designs are popular as range extenders for robots and aerial vehicles.^{xxxv}

9. Triple Combined Cycle SOFC System

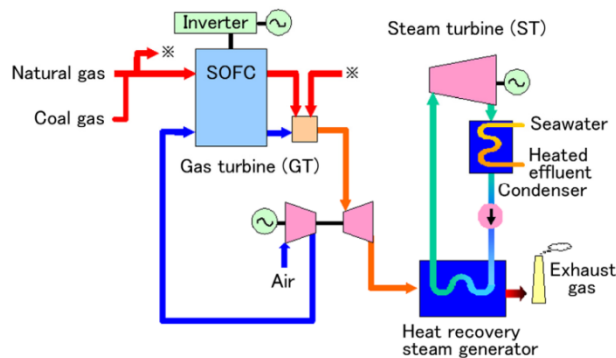
SOFC systems can use hydrocarbon fuels and operate at high temperatures similar to combustion-based power generation systems. In addition to higher efficiency of the SOFC system, CO_2 in the anode exhaust can be captured in downstream condensers since the fuel in the anode side and air in the cathode do not mix as they do in the combustion system. In order to avoid deleterious effects of fuel starvation, SOFC anodes operate fuel-rich. The unspent fuel in the exhaust can be burnt with pure oxygen to have CO_2 and H_2O as the only reaction products. As the water can be condensed at low cost, pure CO_2 can be pressurized and transported to a storage facility for long-term disposal. This process is much easier than the CO_2 -capture in combustion-based power systems, which requires elaborate steps such as membrane gas separation, carbon scrubbing and chemical adsorption technologies for the separation of CO_2 from the flue gas.^{xxxvi}

In addition to stand-alone applications, hybridization of SOFC power systems with combustion systems such as a gas turbine (GT) and combined heat and power (CHP) applications are promising

options that improve the overall efficiency and carbon-capture potential.^{xxxvii} There are several variants of the combination of the SOFC system with the heat engine, usually a GT. Typically, the SOFC acts as a part of the combustor unit, where compressed fuel is fed to anode and air or oxygen is fed to the cathode. Hydrogen from the catalytic oxidation at the inlet of the anode goes to electrochemical reaction in part and generates electricity in the SOFC. After the SOFC, direct combustion of unused fuel and excess hydrogen takes place in a combustor to provide additional heat and utilize all the available energy in the fuel-hydrogen mixture. Combustor exhaust contains only water vapor and carbon dioxide if oxygen is used in the cathode and sent to gas turbine to achieve additional work and electric output.

Several research studies on various combinations SOFC hybrid systems demonstrate that the overall thermodynamic efficiency could be as high as 74% in this configuration. In addition to theoretical analysis, Mitsubishi Heavy Industries (MHI)^{xxxviii} is one of the first companies who have explored the potentials of SOFC systems for large scale power generation since 1980s. In a joint project with New Energy and Industrial Technology Development Organization (NEDO), MHI successfully installed a 200-kW hybrid system featuring SOFC-micro GT technology in 2006 and conducted performance tests in 2007 demonstrating a power output of 229 kW-AC (with SOFC 204 kW/AC and 41 kW/AC with the micro GT) with an overall power efficiency of 52.1% based on lower heating value (LHV) of the fuel. Currently, the company is working to develop an 800-MW class triple combined cycle system, which integrates an SOFC with a utility GT and a steam turbine (ST) (see Figure 6). The SOFC-GT-ST system aims to achieve more than 70% power generation efficiency.^{xxxix}

Figure 6: Triple combined-cycle system



Siemens Westinghouse^{xl} developed and operated a 100-kW tubular SOFC with combined heat and power (SOFC-CHP) system over 29,000 hours with an electrical efficiency of 46% and developing a 250-kW system operating at Kinetics Inc. Facility (in Toronto, Canada) with an electrical efficiency close to 50%.

10. Cost Comparison of Current-Technology SOFCs and Natural Gas Turbines

Recently, SOFC hybrid power systems have received popularity in the literature as hybridization, especially with a gas turbine, that introduces additional opportunities such as improving system flexibility and increasing fuel cell lifetime. Extending the lifetime of fuel cells is crucial in SOFC technology since the cost of the stack is currently in the order of 2–3 k\$/kW.^{xli} For SOFC systems to be economically competitive, lifetimes of 40,000-50,000 hours are required.^{xlii} Battelle^{xliii} has reported the manufacturing costs of 1 kW and 5 kW SOFC for auxiliary power applications using high-volume manufacturing processes at various annual production rates. When the mass production is exercised, 50K units per year, the system cost of a 5kW SOFC with markup becomes \$3,157/kW.

There are two prominent strategies to integrate SOFC with gas turbines: direct thermal coupling which includes at least two power systems (such as SOFC and GT) sharing the same working fluid, and indirect thermal coupling in which the working fluids are separated and only heat is transferred through heat exchange between power systems. Direct thermal coupling is considered as the best suited strategy to the combination of SOFC with GT.

While many of the SOFC-GT studies in the literature are analyzing direct thermal coupling, only a few prototypes of these hybrid systems are available due to the exorbitance cost of SOFC technology; thus, researchers have to rely on mathematical modeling and computer simulation^{xliv} to predict the performance of such systems.

Franzoni et al.^{xlv} modeled a plant in which carbon dioxide is separated. They found that condensing the exhaust steam, which enabled the separation of the CO₂ in the outlet, decreases the system efficiency by 2.8% (from 61.7 to 58.9%). Arsalis^{xlvi} performed a detailed thermo-economic assessment of a 1.5–10 MWe hybrid system and found that for small SOFCs cost minimization is the critical optimization goal, while for large SOFCs efficiency maximization is the main goal.

Thermo-economic analyses' goal is to maximize system efficiencies, minimize irreversibilities or maximize the cost benefit. Various optimization techniques have been practiced in the literature such as single-level modeling (aims to optimize the entire system as a whole) or multi-level modeling (seeks to simultaneously optimize multiple subsystems).

In conventional GT power plants, performances of the first and second law of thermodynamics are low as they are operating under the standard Brayton cycle, where heat input coming from combustion of carbon-based fuels. Conversely, SOFC technology provides better fuel utilization, *ca.* 75%, and better thermal efficiency.

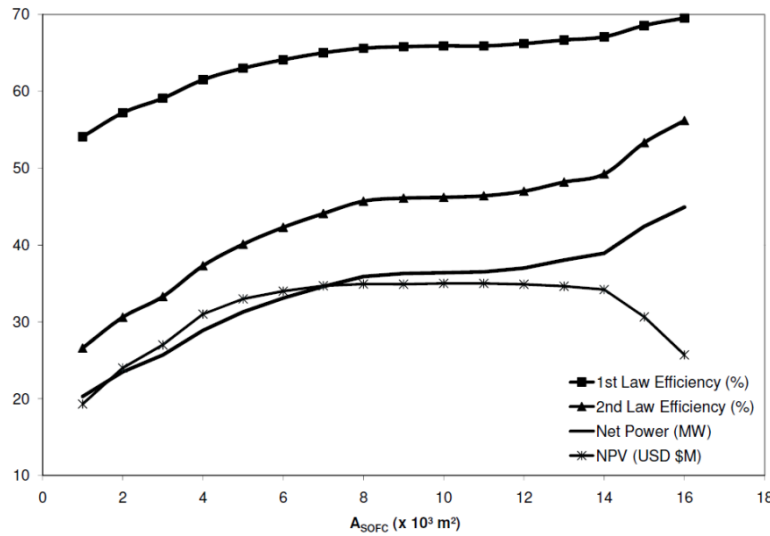
To mitigate the low efficiencies in power plants that are operating on the Brayton cycle, Cheddie^{xlvii} investigates the effects of integrating a SOFC with a 10MW GT power plant. Although the cost of SOFC technology is still a prohibitive factor, the presented cost analysis in Cheddie's study was based on the projected mass production costs when the technology matures.

In the economic analysis, the author assumes the electricity price of USD \$0.05/kWh and the fuel cost of USD \$3.50/MBTU for using natural gas (methane). All costs are converted to net present value (NPV) using a 9% interest rate over a 10-year life cycle. The optimization objective was to

discover the optimum SOFC size by which the NPV is maximized, while supplying sufficient fuel to keep a turbine inlet temperature of 1,400 K.

As the SOFC size increases, the plant efficiency increases asymptotically whereas the capital cost increases almost linearly with SOFC size. Thus, the NPV forms a curve with a peak. By looking at Figure 7, one can see that the NPV reaches a peak of \$34.9 M when a 7,000 m² cell is used. However, 8000 m² is considered to be the optimal size of the SOFC unit required to best match the gas turbine. Efficiencies corresponding to the first and second law for the 8,000 m² cell are 66.2% and 47.0%, respectively. In the mentioned hybrid plant, 23.4 MW out of 37.0 MW is produced by the SOFC component.

Figure 7: Optimization of the SOFC-GT system with respect to NPV



All capital costs and payback periods are shown in Table 3. Note that these numbers only include the cost of adding the SOFC to the power plant. The combustor, turbine and compressors already exist, thus their costs are not taken into account. The fuel cost refers to the annual cost of additional fuel required for the hybrid plant.

Table 3: Cost breakdown for the hybrid plant (USD \$M).

Component	Capital Cost	Annual Gain (Cost)
SOFC Stack	20.1	-
Inverter	1.5	-
Pre-reformer	0.2	-
SOFC Auxiliary	2.0	-
SOFC Total	23.8	-
Heat Exchangers	2.3	-
Fuel Costs	-	(2.3)
Power Gains	-	11.9
NPV	34.9	-
Payback Period	3.3 years	-

The hybrid power plant generates almost four times as much power as the original GT power plant. As a point of comparison, the entire 37-MW hybrid system would cost \$32 M, while an equivalent GT power plant would cost \$9.6 M to produce only 17 MW. All in all, the SOFC hybrid system can decrease the cost of energy to \$0.033/kWh compared to \$0.05/kWh for an equivalent GT system.

Zaccaria et al.^{xlvi} performed economic analysis by comparing a stand-alone, atmospheric SOFC system with a pressurized SOFC gas turbine hybrid. They assume a feed-in tariff (0.14 \$/kWh) to favor an early market penetration of SOFC systems. In their hybrid system, authors assume the stack has to be replaced when the gas turbine reached design power condition. For the stack cost, an optimistic value has been considered⁵. Other economic assumptions/parameters are listed in Table 4.

Table 4: Economic assumptions

Component	Cost
SOFC Stack	400 \$/kW for a stack size of 330 kW
Gas turbine	700 \$/kW
Exhaust gas recuperator	50% turbine cost
SOFC blower	10% stack cost
SOFC inverter	10% stack cost
Annual maintenance	3% capital investment
Electricity price (feed-in tariff)	0.14 \$/kWh
Fuel price	0.1 \$/kg
Discount rate (to actualize cash flow)	0.01

The outcome of analysis proposes that the stand-alone stack is at its most economically advantageous situation when the initial current is at 0.2 A/cm². Further reducing the power density, payback period (PBP) started increasing again, indicating that there is an optimal value of current from an economic point of view. Finally, with a stack cost of \$132,000, 0.5 A/cm² was not economically feasible since the cash flows were negative throughout the system lifetime.

If the stack cost increased to 1,000 \$/kW at 0.5 A/cm², for a total cost of \$330,000, only the two cases at lowest current density gave a positive PBP, equal to 53 years for 0.2 A/cm² and 91 years for 0.1 A/cm². In that scenario, the NPV at 20 years would be negative, respectively -74% and -78% of the initial capital cost (which is now approximately three times higher). At the current stack price of 3,000 \$/kW, which brings the total cost to \$990,000, would not provide positive PBP or NPV for any current density.

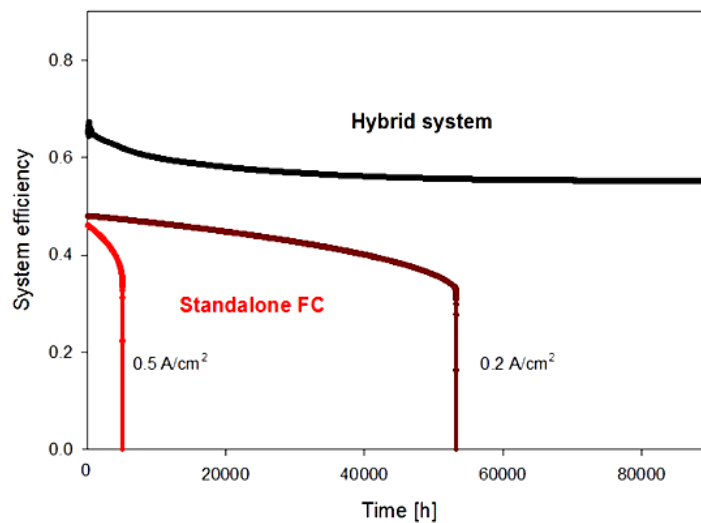
⁵ In 1999, the turbines program funded a study by Rolls Royce with the goal to produce a turbo-generator, which would cost approximately \$400/kW.

Table 5: PBP, NPV, and IRR for the stand-alone stack at constant power with different initial current densities.

Initial current density (A/cm ²)	Lifetime (yr)	Payback period (yr)	NPV (% capital cost)	Internal rate of return
0.5	0.7	-	-538	-0.075
0.4	1.3	26.5	-1.5	0.165
0.3	2.5	7.3	114.2	0.188
0.2	6	6.3	181	0.214
0.1	11.2	11.2	63.8	0.106

However, combining SOFC and gas turbine has improved the resulted hybrid system’s cost and performance, insomuch as the project becomes economically feasible, even at the current stack price of \$3000/kW. This outcome is in line with findings of Cheddie.^{xlix} In Figure 8, the system efficiency through lifetime is compared for the hybrid and stand-alone configurations.

Figure 8: Effect of hybridization with a GT on the system lifetime.



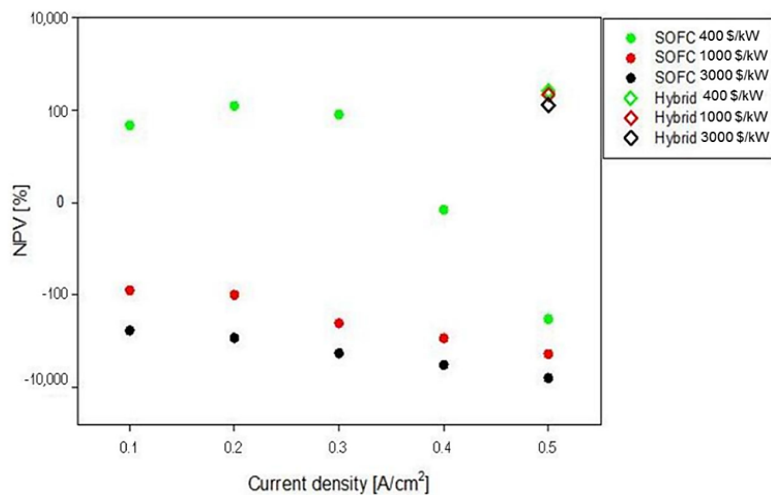
In the hybrid system, the results were not significantly affected by the stack cost. This is due to the stack being replaced once every 11 years and the contribution of gas turbine on the total power production and system efficiency. The PBP is halved in a hybrid configuration with respect to the most advantageous stand-alone case. The very low dependence on stack cost indicates that an early adoption of SOFC technology would be possible at current cost and voltage degradation rate, thanks to the hybridization with gas turbine systems.

Table 6: PBP, NPV, and IRR for the hybrid system.

Stack cost	Stack lifetime (year)	Payback period (year)	NPV (% capital cost)	Internal rate of return
400 \$/kW	11.3	2.9	416	0.33
1,000 \$/kW		3.3	365	0.29
3,000 \$/kW		5.2	189	0.21

Figure 9 demonstrates that stand-alone configuration is only economically feasible if the cost of SOFC stack is \$400/kW. On the other hand, hybridizing SOFC with GT helps the combined system to be practical even with the current stack cost (\$3,000).

Figure 9: NPV trends for stand-alone SOFC and hybrid system with different stack costs.



Meratizaman et al.¹ have investigated the techno-economic advantage of using SOFC-GT technology for residential sector (buildings with 4 floors and 100 m² flat in each floor). They conclude that employing the proposed system in a hot and humid area is more economical with a faster period of return (8.35 years instead of 10.55 years in a colder city).

Rokni^{li} compared the performance of an imaginary repowered steam power plant using different strategies: repowering with a single GT, repowering with two GTs with and without Supplementary Firing (SF) and finally repowering with SOFC. Interestingly, the cost analysis shows that repowering steam power plant with SOFC and hybrid recuperator (HR) is cheaper than using two Siemens SGT5 4000F GTs with small supplementary firing.

Table 7: Total cost of additional required components for repowering.

Plant Configuration	Net Power (MW)	Efficiency (%)	CO ₂ Emission (kg CO ₂ /kWh _e)	Total Cost (\$)	Cost (\$/kW)
Repowered plant with 1 GT	569	47.76	0.44	54,131,342	95
Repowered plant with 2 GT	860	52.88	0.39	108,621,716	126
Repowered plant with SOFC and HR	1003	60.55	0.35	119,863,704	120

In 2008, Arsails^{lii} developed thermo-economic model of a hybrid power plant using a tabular Siemens-Westinghouse-type SOFC with a GT and a ST ranging from 1.5 to 10 MWe. The author considers four different ST cycles: a single-pressure, a dual-pressure, a triple pressure, and a triple pressure with reheat. Moreover, the SOFC cell size is examined. The modelled SOFC-GT-ST hybrid system exhibits better efficiencies (maximum efficiency of 73.8%) that cannot be compared with stand-alone SOFC or SOFC-GT hybrid cycles. The parametric study also revealed some complexities including finding a proper SOFC stack size and proper ST to match the system since GT and ST tend to be inefficient at small scales (e.g., 1.5 MWe).

Sadeghi^{liii} compared two hybrid systems, SOFC-GT and SOFC-GT-ST, with respect to efficiency and the levelized cost of energy (LCOE). Results show that SOFC-GT-ST provides the cheapest electricity per kWh when SOFC input temperature is low (1000 K).

Table 8: Optimization results according to efficiency.

	SOFC input temperature (K)	Efficiency	Annualized Cost (\$/year)	Power Generation (kWh/year)	LCOE (\$/kWh)	Fuel Heat Exchangers mid-temperature (K)	Water Heat Exchangers mid-temperature (K)	Air Heat Exchangers mid-temperature (K)
SOFC -GT	1000	0.543	280,584	14,767,187	0.0190	976	769	990
	1100	0.583	299,870	15,723,885	0.0191	920	937	1088
	1150	0.590	309,630	15,932,997	0.0193	918	1033	1094
SOFC -GT-ST	1000	0.566	290,949	15,580,752	0.0186	848	963	986
	1100	0.596	307,999	16,392,890	0.0187	972	856	1063
	1150	0.599	316,707	16,460,685	0.0192	1092	1012	1099

11. Pathways to Cost Competitive SOFCs

SOFCs have been under investigation for decades, and they are providing higher efficiency vis-à-vis conventional combustion methods. However, its application in the market is confined due to high investment costs and limited lifetime. In this section, we highlight research directions that enhance SOFCs economic viability.

- **Decreasing Costs**

The current manufacturing cost of SOFC stacks is making this technology hard to recommend. Nonetheless, we expect the stack cost to decrease through time by R&D.

Meanwhile, to increase the market penetration and make use of endogenous technology learning (ETL), it is better to combine SOFCs with gas turbines. By doing so, the economic

performance and funding of the entire SOFC supply chain is improved. This pull mechanism ends up with research at universities and research centers, and therefore, decrease the standalone systems' costs.

- **Increasing Lifetime**

SOFCs suffer from a short lifetime (40,000 – 60,000 hours). This short lifetime is due to a progressive performance degradation that leads to cell failure. Also, the brittle nature of ceramics makes them vulnerable to fractures caused by mechanical and thermal stresses; therefore, slight pressure or temperature differences especially in planar design can break the ceramic, leading to cell failure. This physical weakness is critical to investors since it limits the flexibility of the power plant to shut down and start upon demand.

The robustness can be improved by arranging anode, electrolyte, and cathode in tubular form^{liv}. Tubular SOFCs have demonstrated great longevity, thermal cycling robustness, and negligible performance degradation over several years of operation.^{lv} However, this design is harder to produce, and thus, increases the fabrication cost.

- **Decreasing Operating Temperature**

SOFCs are working at high temperature (600 – 1000 °C). Achieving lower operating temperature can simplify the design to a great extent. Issues such as materials instability and interfacial reactions occur less at lower temperatures. Expensive high-temperature materials can be replaced with conventional materials. In planar SOFCs, gas sealing becomes simpler. Moreover, reducing the operating temperature shortens the start-up time, and it reduces the degradation effects of thermal cycling. Finally, low-temperature operation allows better integration with the fuel processing and air preheating parts of the system.^{lvi} However, several limiting factors prevent us from achieving low-temperature SOFCs including the cathode polarization resistance and fuel oxidation on the anode. Because of mentioned limiting factors, the low-temperature operation range appears to be between 500 and 700°C. More research has to be undertaken to address the limiting factors and to further decrease the operating temperature.

- **Enhancing Retrofitability**

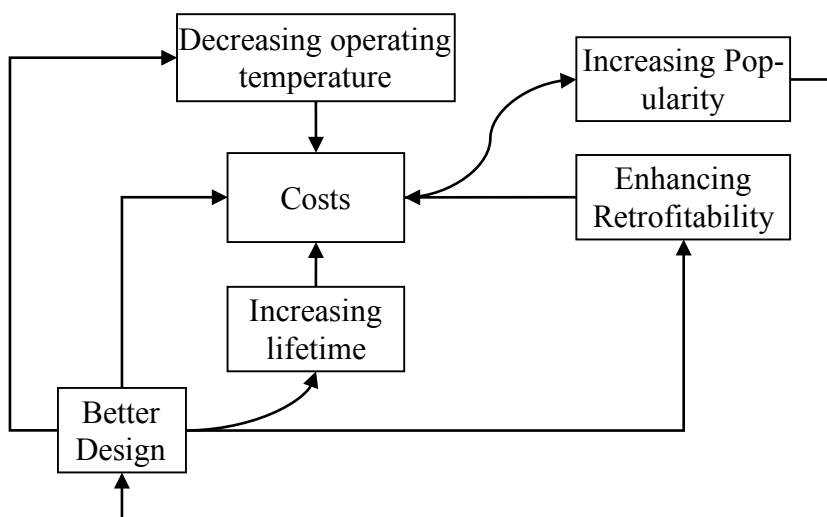
Retrofitting existing power plants will mark a significant step toward the widespread application of SOFC in the near future. Research should be done to understand and assess challenges in retrofitting SOFC stack modules in existing power plants. It is crucial to evaluate power plant off-design performance, required process modifications and operational boundaries based on the existing equipment in the power plant.^{lvii} Multiple challenges exist to retrofit syngas fed SOFCs in existing power plants like cost, process design, material availability, contaminant tolerance, carbon deposition.^{lviii} SOFC systems that are plug-and-play can decrease the overall design cost, improving economic viability.

Figure 10 summarizes the mentioned points in this section. As can be seen in the figure, the high investment cost is the major hindering factor in the popularity of SOFC technology. To lower the cost, more effort has to be put into the design: finding better materials; inventing better mechanical

structure; and designing better manufacturing process. Better designs pave the way for decreasing the investment cost and operating temperature, increase system lifetime and enhance retrofitability. As a direct result of better design, the popularity of SOFC technology increases, and through ETL and more investments better designs will be created.

Figure 10: Summarizing all major factors in the success of the SOFC system.

All links have positive effects.



The good news is that industry and government research agencies are conducting significant research to achieve these goals. To illustrate this, the U.S. Department of Energy provided, during 2016, over \$12 million in grants to develop robust SOFC stacks, highly selective and stable multivariable gas sensors, improvements in electrolyte reliability, low-temperature operation and transformative SOFC technology. The European Commission has also sponsored projects such as cost effective and flexible 3-D printed stacks and next-generation SOFCs. Japan’s New Energy and Industrial Technology Development Organization (NEDO) has launched a demonstration test of a SOFC in Osaka and supported research on SOFC reliability. More important, industry will be ready consumers of these government-supported technological advances to improve their existing SOFC products and introduce them to new markets.

12. Achieving Climate Goals with Solid Oxide Fuel Cells: Policy Recommendations

Governments should give increased priority to achieving carbon capture from natural gas because the expected world-wide growth of natural gas use is considerably larger than the world-wide growth of coal.^{lix} These well-founded expectations should cause energy and climate policy makers to abandon the notion that natural gas is a “transition fuel,” whose use will rapidly diminish as the imperative to reduce GHG emissions increase and as natural gas becomes more expensive due to limited supplies. As discussed above, the supplies of competitive natural gas are likely to extend well beyond the period where energy-sector GHG emissions have to be greatly reduced. The combustion

of the projected natural gas use by the IEA, without CCS, is not compatible with reducing emissions sufficiently to achieve a sustainable energy sector.

As the cost of carbon separation from natural gas, using the current conventional power generating technology, is much higher than carbon separation from coal, and too high for natural gas to be a competitive power-generating fuel (see Section 6 above), an alternative approach is needed to apply CCS to natural gas. The leading alternative approach is the SOFC. SOFCs are the leading alternative approach because 1) their emissions of CO₂ without CCS are relatively low (high efficiency, especially with co-generation); and 2) CO₂ is only comingled with water and unreacted CH₄ resulting in low-cost separation of CO₂. The efficiency losses are minimal compared to the significant efficiency losses when CCS is applied to coal power plants or natural gas turbines.

The primary barrier to the uptake of CCS with SOFCs is the development of a grid-scale SOFC with comparable cost and reliability of natural gas turbines. If SOFCs were a competitive grid scale technology in its own right, quite apart from the ease with which they can be fitted with CCS technology, then the additional cost of CCS would be *de minimis* compared to the cost-prohibitive CCS technologies that are available for coal power plants and natural gas turbines.

While the current research to achieve cost-competitive and reliable SOFCs for grid-scale application is encouraging, these efforts should be significantly increased in order to achieve more rapid technology development and the opportunity to achieve grid-scale commercial application, a necessary step that enables further cost reduction (technology learning, or, learning by doing).

Appendix 1

Overview of Fuel Cell Technologies Other than SOFC

While this paper has discussed the Solid Oxide Fuel Cell (SOFC) in the context of the electric power sector, there are a variety of fuel cell technologies that may better suit a variety of applications, including light-duty motor vehicles. This appendix provides an overview of other fuel cell technologies to place the SOFC into the context as a technology that is best suited for generating electricity in stationary settings.

All fuel cells are static electrochemical energy conversion devices that convert chemical energy stored in fuel directly into electrical power. In the simplest systems, the fuel is hydrogen, the oxidant is oxygen and the only by-product is water. The whole conversion operation involves motion of charge carriers (ions and electrons on different paths) and their “mostly catalyzed” reactions to each other. Thus, the device has no other moving parts and therefore very quiet.

Fuel cells are categorized mostly according to their electrolyte and fuels.^{lx} There are six different fuel cell systems. Some of them could not find wide spread application due to their inherent shortcomings whereas others still offer a viable potential for the future. They are:

Proton exchange membrane fuel cell (PEMFC): Proton exchange membrane FCs (sometimes called polymer electrolyte membrane FCs) utilize a Teflon like, proton conducting polymer film as their electrolyte. This electrolyte is an insulator for electron flow. PEMFC uses a water-based, acidic polymer membrane (Nafion by DuPont or derivatives^{lxi} as the electrolyte and platinum-catalyzed electrodes. It uses pure hydrogen, but also reformed natural gas, removing carbon monoxide. Its operative temperature is below 100 °C. Secondly, HT-PEMFC (high temperature PEMFC) is a PEMFC obtained by changing the electrolyte from a water-based to a mineral acid- based system. It operates up to 200 °C.^{lxii}

The advantages of the PEM fuel cell are its higher power density and quick start up for automotive vehicles. The low operating temperature makes the technology competitive in transportation and commercial applications like laptop computers, bicycle and mobile phones. The commercial electrolyte Nafion needs to be hydrated to function properly that necessitates temperatures lower than 100°C. It is temperature where the reaction product is in liquid form and needs to be extracted through the porous electrodes. The search is for polymer electrolyte that will operate above 100°C possibly around 120°C. Other major drawbacks of the PEM fuel cell are its lower operating efficiency (40–45%) and use of high cost platinum catalyst which is also intolerant to carbon monoxide.

Direct alcohol (MeOH and EtOH) fuel cells: These are derivations of the PEM fuel cell where liquid methanol or ethanol are being used instead of gaseous hydrogen. They use Nafion electrolyte and a catalyst like PEM FC. The main advantage of this type is the elimination of the need for an external reformer. Methanol or ethanol are oxidized in water to produce hydrogen ion and electron. The main disadvantage is the crossover of the liquid fuel through the electrolyte to cathode side which lowers the system efficiency.

Formic acid (HCOOH), is another small organic molecule that has also been used as a liquid fuel with PEM electrolyte. In the so called direct formic acid fuel cell, the advantage is that the fuel does

not crossover the Nafion electrolyte resulting in a higher system efficiency than the direct methanol fuel cell.

Alkaline fuel cell (AFC): Alkaline fuel cells are one of the earliest fuel cells to find practical applications. NASA used them for space explorations due to their high efficiency (around 70%) and their relatively low operating temperatures (70-100°C). Aqueous solution of KOH is the electrolyte in alkaline fuel cells and OH⁻ ions are transported from cathode, where CO₂ free oxygen is fed into the system, to the anode where hydrogen fuel is supplied. Water is produced at the anode.

Its low operating temperatures gives it the advantage of quick start and stop cycles. One major disadvantage is the sensitivity of the electrolyte solution to CO₂. Another disadvantage is the fact that the strongly alkaline electrolyte solution is corrosive to most of the container materials which limits the life of the fuel cell.

Direct borohydride fuel cell (DBFC): Borohydride fuel cells are a type of alkaline fuel cell. In these kind of fuel cells sodium or potassium borohydride releases their hydrogen in contact with water by catalytic decomposition thereby being oxidized to NaBO₂ or KBO₂. Oxygen or air is the oxidant. It operates at ~70°C and does not require an expensive Pt catalyst. This type of FC is still under development and is attractive because of its high open circuit cell potential of 1.64 eV. Currently, sodium borohydride is very expensive and its recycling is still an issue of intensive research.

Phosphoric acid fuel cell (PAFC): Phosphoric acid fuel cells operate by hydrogen ion transport from anode through hot (~200°C) phosphoric acid to the cathode where oxygen or air is fed to the cell. Compared to the other liquid electrolytes, since Phosphoric acid does not necessitate water to operate, they can run at higher temperatures. The high operating temperatures bring in certain advantages: It is more tolerant to impurities in the reformed hydrogen fuel than PEM fuel cells are. Its operation temperature allows CO impurity up to 1.5%. Therefore, they can use reformed hydrocarbons as fuels (Mekhelif et al 2012). The hot water exhaust at the cathode can be used for co-generation of hot water or electricity. At lower temperatures, its ionic conductivity is low and its Pt catalyst gets poisoned by CO. Its cost is high due to the Pt catalyst, however, it has been commercially employed at several locations world-wide. Electrical efficiency of PAFC is on the order of 40-50%, and with co-generation it goes up to 85%.^{lxiii}

Molten carbonate fuel cell (MCFC): Molten carbonate fuel cells are one of the high temperature fuel cells which enjoy high operating efficiencies on the order of 50-60%, no need for expensive metal catalysts, and the possibility of using many different types of fuels. However, the fuels should be without Sulphur since these fuel cells are sensitive to even small amounts of Sulphur. In the cells the molten carbonate is in an intimate contact with the porous ceramic electrodes. Carbonate ion (CO₃²⁻) is the charge carrier. Hydrogen or hydrocarbons are fed at the anode, air or oxygen is fed at the cathode. CO₂ is circulated and reused between anode and cathode through an outside duct to supply the electrolyte with carbonate ions. Just like alkaline fuel cells and phosphoric acid fuel cells MCFCs also have a high ionic conductivity (i.e. >1 S/cm) at operating temperatures. The associated leakage problems in fuel cells with liquid electrolyte is important.

Appendix 2

Sabancı University Materials Research

As discussed above, SOFCs are the major high temperature fuel cell system which is well adapted for distributed power generation for rural areas with no access to power grid. Since they are noise-free and low maintenance, it is also suitable for military and disaster-relief applications.^{lxiv} They used heavily doped (mix)metal oxides as electrolyte and matching electrodes. The most common charge carrier is O^{2-} , however, there is significant research devoted also to proton conducting ceramics that operate at elevated temperatures. The elevated temperatures allow the use of a selection of hydrocarbon fuels as long as they are desulfurized. H_2 and CO are the most common fuels which react with the oxygen ion at the anode side to produce H_2O or CO_2 . The natural by-product is heat which is again used in generating electricity with the help of gas turbines. The combined heat and power (CHP) efficiencies are on the order of 70-80%. The system efficiencies on the order of 50% are possible.^{lxv} The most common electrolyte used today is yttria stabilized zirconia (YSZ) due its high and pure ionic conductivity, mechanical robustness, and chemical stability.^{lxvi} Although lately, scandium stabilized zirconia is more commonly preferred for intermediate temperature (650°C) range since it has a higher ionic conductivity.

The disadvantages of the SOFCs are the high operating temperature which are necessitated by the low ionic conductivities due to ionic diffusion in the solid state of the current electrolytes at lower temperatures. Another disadvantage is the long start-up and power-down cycle times. High temperatures also necessitate electrodes with chemical and thermal compatibility with the electrolyte used. The area specific resistance values required for commercialization necessitates gas-tight solid oxide electrolytes with thicknesses on the order of 10-30 micrometer.^{lxvii} Such thin ceramic sheets need to be supported on a porous electrode, anode or cathode. Sintering 30 micrometer or thinner gas-tight electrode requires temperatures in excess of 1200°C. At the same temperature the support electrode must remain porous with interconnected porosity, must not react with the electrolyte, and must have a matching thermal expansion coefficient for the temperature gradient down to room temperature. For solid oxide fuel cells that operate at temperatures in excess of 800°C, special materials also need to be considered as bipolar plates to separate the stacks, allow electrical contact and seal the assembly.

Research on ceramic solid membranes that conduct protons is focused on perovskite structured zirconia and ceria-based systems.^{lxviii} Although the open circuit voltage values are good, the low current densities provides a challenge yet.^{lxix} It is claimed that $BaZr_xY_zO_{3-d}$ has appreciable ionic conductivity (0.01 S/cm) at 500°C.^{lxx}

Not so High Temperature Fuel Cells: The ‘high temperature’ fuel cells that are offering a potential for development are based on solid oxide electrolytes and their matching ceramic electrodes, shortly called solid oxide fuel cells (SOFCs). Although they are categorized as ‘high temperature’ fuel cells, the quest for solid oxide fuel cells is to lower the operation temperatures (to below 650°C) where common industrial materials, like steel, can be used to seal and contain the cell stacks.

Currently, industrial scale solid oxide fuel cell operates at or around 1000°C. These commercial fuel cells are based on an oxygen ion (O^{2-}) conducting yttria stabilized zirconia (YSZ; (Y)ZrO₂) electrolyte. Their electrodes are mixtures of YSZ and other complex oxides with mixed conductivities.

Westinghouse, Kyocera, and Mitsubishi successfully demonstrated that stationary solid oxide fuel cells are a reality and are here to stay.

The quest for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC): There are several systems that are investigated as potential intermediate temperature fuel cell electrolytes. Intermediate temperatures are accepted to be around 500-650°C. Most of studies are focusing on fluorite or perovskite type oxides.^{lxxi} These crystal types are known to be very tolerant to lattice defects. They can accommodate large concentrations of oxygen vacancies. Therefore, these solid oxides have relatively high diffusion coefficients at intermediate temperatures. These diffusion coefficients come in structures with relatively weak bonding and an extensive defect structure. However, there are additional complications that come with weak bonding and defective structures: (i) They have relatively high thermal expansion coefficients. In order to match the thermal expansion coefficients of the electrolyte and the electrodes, oxides with similar structures but altered chemistries are needed; (ii) The interfaces between electrolytes and their matching electrodes become unstable and the interdiffusion of cacophony of cations between the components of the cell becomes facilitated (an unwelcomed reality). Some of the latest research efforts focus mostly on finding solution on such unwanted reactions.

Around mid 1990's, mixed cation oxide electrolytes for SOFCs were introduced that would provide the ionic conductivities (0.1 S/cm) around 650°C. It is usually assumed that one needs an area specific resistivity of about 0.1-0.15 Ohm/cm² for commercialization. That would again force the SOFC electrolyte to be of a thickness on the order of few tens of micrometer (~30 micrometer or less). Sintering and densifying these low temperature thin electrolyte supported on a porous electrode is a major challenge for the academia and industry. One of these oxide electrolytes with remarkable ionic conductivity at intermediate temperatures is lanthanum, strontium, gallium, magnesium oxide (LSGM) that is based on a perovskite structure with more than 20% oxygen ion deficiency in its crystal lattice.^{lxxii lxxiii lxxiv} Onel *et al*^{lxxv} showed that LSGM electrolyte that is only 5 micrometer thick can be sintered to full density (gas tightness) on a porous SDC/NiO anode at temperatures around 1250°C. In the meantime, the interconnected nature of the anode porosity was preserved (Figure A2.1).

One of the major problems with the four-cation (La, Sr, Ga, and Mg) oxide system of LSGM is its reactions with its most suitable anode material, SDC/NiO. At sintering temperatures, La in LSGM reacts with the Ni in the anode cermet to give LaNiO₃ which is an insulator. To stop the interface reactions Onel *et al* suggested a 3-micrometer thick dense protective layer of LDC.^{lxxvi} Their results showed that La doped ceria stopped the Ni diffusion to LSGM electrolyte and the consecutive nikelate formation (Figure A2.2).^{lxxvii}

On the other side of the LSGM electrolyte, the cathode materials are also mixed cation oxides, e.g. BSCF or SCF. Ekinici (investigated their stability against the LSGM electrolyte in a temperature range that also includes the possible operating temperatures of the LSGM based SOFC (700-1100°C). She reported that neither SCF nor the BSCF are stable against LSGM in oxidizing environment in the long run.

Figure A2.1: SEM-Secondary Electron Detector image of the anode-electrolyte cross section which was sintered at 1250°C for 2 hours^{lxxviii}

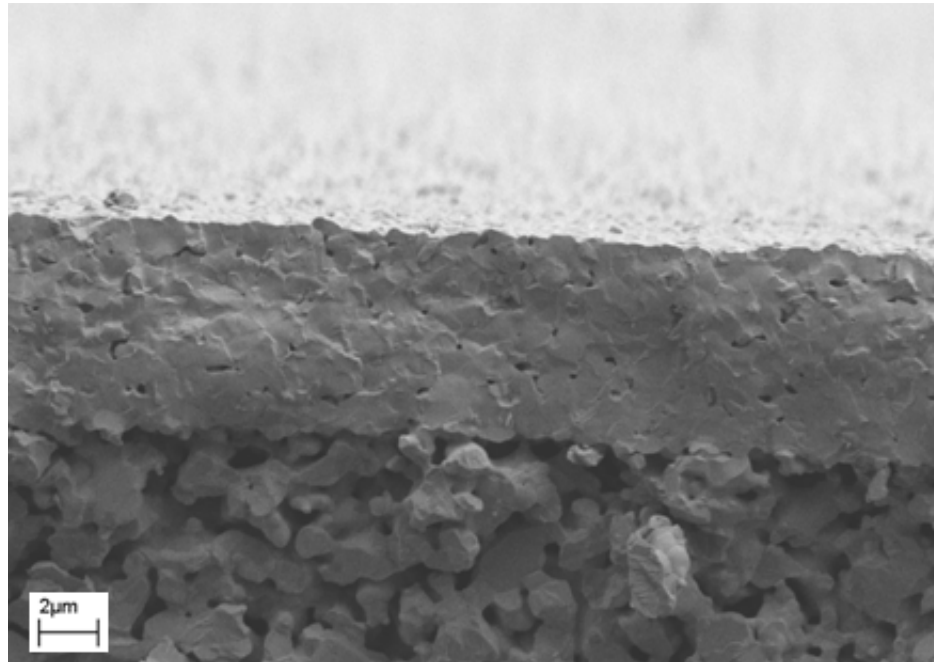
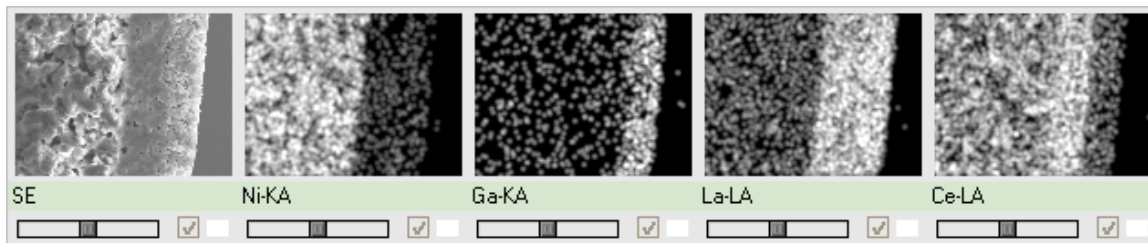


Figure A2.2 EDS-map of anode-LDC-LSGM assembly. LDC was sintered first, then LSGM deposited and sintered. Nickel, gallium, lanthanum and cerium signals are shown.



There are also other candidates for IT-SOFCs however, several of these system have serious stability issues when it comes to long operating times at the indicated temperature.

Bismuth oxide (Bi_2O_3) based electrolytes show very high ionic conductivities at relatively low temperatures for SOFCs.^{lxxix} It has been found that the conduction characteristics of α -phase is electronic, whereas conductance characteristics of β , γ and δ -phases are ionic.^{lxxx} Although stable between 730°C and 804°C, δ -phase has the highest ionic conductivity, such as 2.3 S/cm around 800°C.^{lxxxi} It has been shown that δ - Bi_2O_3 remains stable by partial cation doping for bismuth.^{lxxxii} However, bismuth oxides cannot be utilized as stand-alone electrolytes because of their thermodynamic instability in the presence of a reducing gas (e.g. H_2 or CH_4) atmosphere.^{lxxxiii}

Another electrolyte candidate for intermediate temperature SOFCs (IT-SOFCs) is doped ceria-based systems. Typical doping agents are samarium oxide or gadolinium oxide. Much higher conductivity values compared to stabilized zirconia at lower temperatures makes them attractive electrolytes.^{lxxxiv} The main problem of doped ceria electrolytes is the reduction of Ce^{4+} to Ce^{3+} at low oxygen partial pressures (e.g. in reducing atmospheres). This reduction result in prominent electronic conductivity at IT-SOFC operation temperatures ($>650^{\circ}C$).^{lxxxv} Bilayer electrolyte/protective layer usage could be a solution for stopping the electron conduction within the doped ceria electrolytes. However, although electronic conductivity (i.e. passage of electrons through the ceramic) is a problem for ceria ceramics as an electrolyte, it makes them suitable as electrode materials. There are several ceria-based electrodes and barrier layers used in several intermediate temperature range SOFCs.^{lxxxvi}

As the number of cations in the mixed oxide electrolyte increases, the possibility of incorporating larger concentrations of oxygen vacancies become possible. The increased oxygen ion concentration has a direct influence on the ionic conductivity as the ionic diffusion process is facilitated by vacant oxygen sites in the lattices. However, as the base crystal structure becomes more defective, the chemical compatibility between the components of the cell at operating temperatures raises a bigger issue. Formation of electrical isolating oxide phases at the interface between the electrodes and the electrolyte decreases the cell efficiency and life expectancy of the cell.

An alternative for intermediate temperature SOFCs are the so-called nanocomposite fuel cells that are composed of nanometer-sized ionic conductor oxide particles and an amorphous carbonate matrix.^{lxxxvii} These electrolytes are basically a 3Dimensionally interconnected mixture of molten carbonate fuel cell and solid oxide fuel cell electrolytes. The rather high ionic conductivities achieved in this composite are believed to be due to conduction neither in the oxide backbone nor in the amorphous carbonate matrix but through the interfaces which are dubbed as superionic conduction highways by Zhu and co-workers.^{lxxxviii} The nanostructured composite provides an increased amount of these fast diffusion pathways in the microstructure as shown by Shawuti and Gulgun. It was suggested that the fast-diffusion pathways are a direct result of the interactions between the surface charges of the oxide particles and the salt molecules in the amorphous carbonate matrix above the glass transition temperature of the matrix (Shawuti and Gulgun 2014, Shawuti et al 2016). Shawuti introduced a model for these nanocomposite electrolyte which is a rendering of the so-called “soggy sand” electrolytes in liquid electrolytes of ion batteries (Bhattacharya and Mayer). Benli et al. revealed that by modifying the surface charges of the oxide nanoparticles, one can tailor the ionic conductivity in the solid composite to a certain extend. Shawuti and coworkers’ proposed model for these intermediate temperatures nanocomposite electrolytes relies on the dissociation of the salt molecules of the carbonate matrix by the electrostatic interaction with the surface charges of the oxide particles.^{lxxxix}

References

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- ⁱ International Energy Agency, *Energy Technology Perspectives 2017*, June 2017
- ⁱⁱ International Energy Agency, *World Energy Outlook 2017*, Paris, November, 2017
- ⁱⁱⁱ International Energy Agency, *World Energy Outlook 2017*, Paris, November, 2017
- ^{iv} International Energy Agency, *World Energy Outlook 2017*, Paris, November, 2017
- ^v International Energy Agency, *World Energy Outlook 2017*, Paris, November, 2017
- ^{vi} Stram, Bruce, “Key Challenges to Expanding Renewable Energy, *Energy Policy*, Vol. 96, pp 728-734, 2016
- ^{vii} Khatib, H and Carmine Difiglio, “Economics of Nuclear and Renewables, *Energy Policy*, Vol. 96, pp 740-750, 2016
- ^{viii} International Energy Agency, *World Energy Outlook 2017*, Paris, November, 2017
- ^{ix} Kanniche, M., Gros-Bonnivard, R., Jaud, P., Valle-Marcos, J., Amann, J. M., & Bouallou, C., Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO₂ capture. *Applied Thermal Engineering*, 30(1), 53-62, 2010
- ^x Source of Figure 2: National Energy Technology Laboratory, Chemical Looping Combustion, <https://www.netl.doe.gov/research/coal/energy-systems/advanced-combustion/clc>
- ^{xi} Kanniche, M., Gros-Bonnivard, R., Jaud, P., Valle-Marcos, J., Amann, J. M., & Bouallou, C., Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO₂ capture. *Applied Thermal Engineering*, 30(1), 53-62, 2010
- ^{xii} Elwell, L. C., & Grant, W. S.. Technology options for capturing CO₂, *Power Magazine*, 150(8), 60, 2006
- ^{xiii} Bjorn Nykvist, “Ten times more difficult, Quantifying the carbon capture and storage challenge,” *Energy Policy*, vol. 55 pp. 683-639, 2013
- ^{xiv} Steen M. Greenhouse gas emissions from fossil fuel fired power generation systems. *Institute for Advanced Materials, Joint Research Centre, European Commission*, 2000
- ^{xv} IEA, *Resources to Reserves*, Paris, 2013, p. 176
- ^{xvi} U.S. EIA, *World Shale Resource Assessment*, September 24, 2015
- ^{xvii} IEA, *World Energy Outlook 2016*, Paris, 2016, p. 181
- ^{xviii} IEA, *World Energy Outlook 2016*, Paris, 2016, p. 249
- ^{xix} *Modern Power Systems*, 2008
- E.On UKm 2007
- ^{xx} GHG, IEA. CO₂ capture as a factor in power station investment decisions, IEA GHG (IEA Greenhouse Gas R&D Programme) Report 2006/8, 2006.
- ^{xxi} <https://www.bloomenergy.com/solutions/energy-server-platform>
- ^{xxii} <http://www.bosch-presse.de/pressportal/de/en/bosch-presents-power-generating-heating-system-based-on-fuel-cell-technology-42124.html>
- ^{xxiii} <http://convion.fi/products/>
- ^{xxiv} <http://www.elcogen.com/#network>
- ^{xxv} <https://www.mhps.com/products/sofc/>
- ^{xxvi} <https://www.energy.gov/fe/why-sofc-technology>
- ^{xxvii} Kendall, S. C. (2003). High temperature solid oxide fuel cells: fundamentals, design and applications. Oxford.
- ^{xxviii} Adams, Thomas A, Jake Nease, David Tucker, and Paul I Barton. “Energy Conversion with Solid Oxide Fuel Cell

Systems: A Review of Concepts and Outlooks for the Short- and Long-Term.” *Industrial & Engineering Chemistry Research* 52(9): 3089–3111. <http://dx.doi.org/10.1021/ie300996r>, 2013.

^{xxxix} Electrochemical Society Interface, Fall 2009

^{xxx} Adams et al, 2013

^{xxxix} Goodenough, J. (2000). Ceramic technology: oxide-ion conductors by design. *Nature*, 821-3.

^{xxxii} J. Hanna, W. L. (2014). Fundamentals of electro- and thermochemistry in the anode of solid-oxide fuel cells with hydrocarbon and syngas fuels. *Progress in Energy and Combustion Science*, 74-111.

^{xxxiii} Buonomano, Annamaria et al. 2015. “Hybrid Solid Oxide Fuel Cells-Gas Turbine Systems for Combined Heat and Power: A Review.” *Applied Energy* 156: 32–85. <http://dx.doi.org/10.1016/j.apenergy.2015.06.027>.

^{xxxiv} Przybylski, Kazimierz et al. 2014. “Oxidation Properties of the Crofer 22 APU Steel Coated with La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ for IT-SOFC Interconnect Applications.” *Journal of Thermal Analysis and Calorimetry* 116(2): 825–34. <http://link.springer.com/10.1007/s10973-013-3594-1>.

^{xxxv} Kendall, K, B Liang, and M Kendall, “Microtubular SOFC (mSOFC) System in Mobile Robot Applications” *ECS Transactions* 78(1): 237–42, 2017.

^{xxxvi} Tan, Yuting et al., “Property Impacts on Carbon Capture and Storage (CCS) Processes: A Review.” *Energy Conversion and Management* 118: 204–22. <http://dx.doi.org/10.1016/j.enconman.2016.03.079>. 2016

^{xxxvii} Fuel Cell Handbook, seventh ed., Office of Fossil Energy, National Energy Technology Laboratory, Morgantown, West Virginia, November, 2004.

^{xxxviii} Kobayashi, Yoshimuro et al. “Recent Progress of SOFC-GT Combined System with Tubular Type Cell Stack at MHI,” *ECS Transactions*, 57 (1), 2013.

^{xxxix} Kobayashi, Yoshimuro et al. “Extremely high-efficiency thermal power system-solid oxide fuel cell (SOFC) triple combined-cycle system.” *Mitsubishi Heavy Industries Technical Review* 48 (3): 9-15, 2011

^{xl} “Siemens celebrates one-year anniversary of SOFC generator in Italy,” *Fuel Cells Bull.* September (2006)

^{xli} Colantoni, Andrea, et al. “Economical analysis of SOFC system for power production.” *Computational Science and Its Applications-ICCSA 2011*: 270-276. 2011

^{xlii} Hawkes Adam and Brett Dan, “Fuel Cells for Stationary Applications”, *IEA ETSAP*, 2013

^{xliii} Battelle, “Manufacturing Cost Analysis of 1 kW and 5 kW Solid Oxide Fuel Cell (SOFC) for Auxiliary Power Applications”, *U.S. Department of Energy*, DOE Contract No. DE-EE0005250, 2014

^{xliv} Bao, Cheng, et al. “Multi-level simulation platform of SOFC–GT hybrid generation system.” *international journal of hydrogen energy* 35(7): 2894-2899. 2010

^{xliv} Franzoni, A., et al. “Thermoeconomic analysis of pressurized hybrid SOFC systems with CO₂ separation.” *Energy* 33(2): 311-320. 2008

^{xlvi} Arsalis A. “Thermoeconomic modeling and parametric study of hybrid SOFC–gas turbine–steam turbine power plants ranging from 1.5 to 10MWe.” *Journal of Power Sources* 181(2): 313-26. 2008

^{xlvi} Cheddie, Denver F. “Integration of a solid oxide fuel cell into a 10 MW gas turbine power plant.” *Energies* 3.4: 754-769. 2010

^{xlvi} Zaccaria, Valentina et al. “Gas turbine advanced power systems to improve solid oxide fuel cell economic viability.” *Journal of the Global Power and Propulsion Society* 1 (2017): U961ED.

^{xlvi} Cheddie, Denver F. “Integration of a solid oxide fuel cell into a 10 MW gas turbine power plant.” *Energies* 3.4: 754-769. 2010

^l Meratizaman, Mousa, Sina Monadizadeh, and Majid Amidpour. “Techno-economic assessment of high efficient energy production (SOFC-GT) for residential application from natural gas.” *Journal of Natural Gas Science and Engineering* 21: 118-133. 2014

-
- ^{li} Rokni, Masoud. "Performance comparison on repowering of a steam power plant with gas turbines and Solid Oxide Fuel Cells." *Energies* 9.6: 399. (2016)
- ^{lii} Arsalis A. "Thermoeconomic modeling and parametric study of hybrid SOFC–gas turbine–steam turbine power plants ranging from 1.5 to 10MWe." *Journal of Power Sources* 181(2): 313-26. 2008
- ^{liii} Sadeghi, S. "Multi-objective optimization of two hybrid power generation systems for optimum selection of SOFC reactants heat exchangers mid-temperatures." *Iranian Journal of Hydrogen & Fuel Cell* 3 (2017): 175-188.
- ^{liv} J. Milewski, & W. Budzianowski, "Recent key technical barriers in solid oxide fuel cell technology" *Archives of Thermodynamics*, 35(1): 17-41, (2014).
- ^{lv} DiGiuseppe, G., "High power density cell development at Siemens Westinghouse" Solid Oxide Fuel Cells IX, SC Singhal and J. Mizusaki, eds., The Electrochemical Society Proceedings Series, Pennington, NJ, 322–332, (2005).
- ^{lvi} Carter, J. D., Cruse, T. A., Ingram, B. J., & Krumpelt, M., "Factors limiting the low temperature operation of SOFCs". Handbook of Fuel Cells (2010).
- ^{lvii} A. T. Thattai, V. D. W. M. Oldenbroek, L. Schoenmakers, T. Woudstra, & P.V. Aravind, "Towards retrofitting integrated gasification combined cycle (IGCC) power plants with solid oxide fuel cells (SOFC) and CO₂ capture—A thermodynamic case study" *Applied Thermal Engineering*. 114:170-185, (2017).
- ^{lviii} T. M. Gür, "Comprehensive review of methane conversion in solid oxide fuel cells: prospects for efficient electricity generation from natural gas". *Progress in Energy and Combustion Science*. 54:1-64, (2016).
- ^{lix} IEA, World Energy Outlook 2016, Paris, 2016, p. 249
- ^{lx} A. Kirubakaran, Jain, S., and Nema, R.K., "A review on fuel cell technologies and power electronic interface". *Renewable and Sustainable Energy Reviews*. 13:2430–2440 (2009).
- ^{lxi} B.C.H. Steele and A. Heinzl, Materials for Fuel Cell Technologies," *Nature* 414, 345-352, (2001).
- ^{lxii} Lucia, Umberto., "Overview on fuel cells", *Renewable and Sustainable Energy Reviews*. 30. 164–169 (2014)
- ^{lxiii} S. Mekhilef, R. Saidur, and A. Safari, "Comperative study of different fuel cell technologies" *Renewable and Sustainable Energy Reviews* 16, 981–89, (2012).
- ^{lxiv} S. Mekhilef, R. Saidur, and A. Safari, "Comperative study of different fuel cell technologies" *Renewable and Sustainable Energy Reviews* 16, 981–89, (2012).
- ^{lxv} A. Kirubakaran, Jain, S., and Nema, R.K., "A review on fuel cell technologies and power electronic interface". *Renewable and Sustainable Energy Reviews*. 13:2430–2440 (2009).
- ^{lxvi} S. Mekhilef, R. Saidur, and A. Safari, "Comperative study of different fuel cell technologies" *Renewable and Sustainable Energy Reviews* 16, 981–89, (2012).
- ^{lxvii} B.C.H. Steele and A. Heinzl, Materials for Fuel Cell Technologies," *Nature* 414, 345-352, (2001).
- ^{lxviii} H.I. T, Yajima, H. Kazeoka, T. Yogo, "High temperature proton conducting oxides and their applications to solid electrolyte fuel cells and steam electrolyzer for hydrogen production," *Solid State Ionics*, **28–30** 573–578 (1988).;
- T. YAJIMA, H. KAZEOKA, T. YOGO, and H. IWAHARA, "Proton conduction in sintered oxides based on CaZrO₃," *Solid State Ionics*, **47** [3–4] 271–275 (1991).;
- T. Yajima, "Protonic conduction in SrZrO₃-based oxides," *Solid State Ionics*, **51** [1–2] 101–107 (1992).;
- D. Shima and S.M. Haile, "The influence of cation non-stoichiometry on the properties of undoped and gadolinia-doped barium cerate," *Solid State Ionics*, **97** [1–4] 443–455 (1997).; B.C.H. Steele and A. Heinzl, Materials for Fuel Cell Technologies," *Nature* 414, 345-352, (2001).
- H. Iwahara, T. Esaka, T. Sato, and T. Takahashi, "Formation of high oxide ion conductive phases in the sintered oxides of the system Bi₂O₃-Ln₂O₃ (Ln = La or Yb)," *J. Solid State Chem.*, **39** [2] 173–180 (1981).;
- H. IWAHARA, "Oxide-ionic and protonic conductors based on perovskite-type oxides and their possible applications," *Solid State Ionics*, **52** [1–3] 99–104 (1992).;

-
- H. IWAHARA, T. YAJIMA, T. HIBINO, K. OZAKI, and H. SUZUKI, "Protonic conduction in calcium, strontium and barium zirconates," *Solid State Ionics*, **61** [1–3] 65–69 (1993).;
- H. Uchida, "Relation between proton and hole conduction in SrCeO₃-based solid electrolytes under water-containing atmospheres at high temperatures," *Solid State Ionics*, **11** [2] 117–124 (1983)).
- ^{lxxix} A. Kirubakaran, Jain, S., and Nema, R.K., "A review on fuel cell technologies and power electronic interface". *Renewable and Sustainable Energy Reviews*. 13:2430–2440 (2009).
- ^{lxxx} B.C.H. Steele and A. Heinzl, Materials for Fuel Cell Technologies," *Nature* **414**, 345-352, (2001).
- ^{lxxxi} J B Goodenough, "Electronic and ionic transport properties and other physical aspects of perovskites" *Rep. Prog. Phys.* **67** 1915 (2004).
- ^{lxxxii} J. W. Fergus, Electrolytes for solid oxide fuel cells, *Journal of Power Sources*, 2006, **162**, 1, 30 (2006).
- ^{lxxxiii} T. Ishihara, "Chapter 79. Novel electrolytes operating at 400–600 C," *Fuel Cell Handbook Vol. 4*, pp. 1109–1122 (2003)
- ^{lxxxiv} J.B. Goodenough, "Oxide-Ion Electrolytes," *Annu. Rev. Mater. Res.*, **33** 91–128 (2003).
- ^{lxxxv} C. Oncel, B. Ozkaya, and M. A. Gulgun, "X-Ray Single Phase LSGM at 1350C", *J. Euro. Ceram. Soc.*, **27** (2-3): 599-604 (2007).
- ^{lxxxvi} C. Oncel and Mehmet Ali Gulgun, "Interface Reactions Between the Anode and Lanthanum Gallate-type Electrolyte in Solid Oxide Fuel Cells," to be submitted to *J. Euro. Ceram Soc.*, March 2018.
- ^{lxxxvii} C. Oncel and Mehmet Ali Gulgun, "Interface Reactions Between the Anode and Lanthanum Gallate-type Electrolyte in Solid Oxide Fuel Cells," to be submitted to *J. Euro. Ceram Soc.*, March 2018.
- ^{lxxxviii} C. Oncel and Mehmet Ali Gulgun, "Interface Reactions Between the Anode and Lanthanum Gallate-type Electrolyte in Solid Oxide Fuel Cells," to be submitted to *J. Euro. Ceram Soc.*, March 2018
- ^{lxxxix} A.J. Jacobson, "Materials for Solid Oxide Fuel Cells," *Chem. Mater.*, **22** [3] 660–674 (2010). ; A. Kirubakaran, S. Jain, R. K. Nema, "AReview on Fuel cell technologies and power electronic interface," *Renewable and Sustainable Energy Reviews* 13, 2430–2440, (2009).
- T. Takahashi, H. Iwahara, and T. Arao, "High oxide ion conduction in sintered oxides of the system Bi₂O₃-Y₂O₃," *J. Appl. Electrochem.*, **5** [3] 187–195 (1975).;
- H.A. Harwig and A.G. Gerards, "Electrical properties of the α , β , γ , and δ phases of bismuth sesquioxide," *J. Solid State Chem.*, **26** [3] 265–274 (1978).)
- ^{lxxx} T. Takahashi and H. Iwahara, "High oxide ion conduction in sintered oxides of the system Bi₂O₃-WO₃," *J. Appl. Electrochem.*, **3** [1] 65–72 (1973)).
- ^{lxxxii} J.B. Goodenough, "Oxide-Ion Electrolytes," *Annu. Rev. Mater. Res.*, **33** 91–128 (2003).
- ^{lxxxiii} H.A. Harwig and A.G. Gerards, "Electrical properties of the α , β , γ , and δ phases of bismuth sesquioxide," *J. Solid State Chem.*, **26** [3] 265–274 (1978).)
- M.J. Verkerk, K. Keizer, and A.J. Burggraaf, "High oxygen ion conduction in sintered oxides of the Bi₂O₃-Er₂O₃ system," *J. Appl. Electrochem.*, **10** [1] 81–90 (1980).;
- M.J. Verkerk and A.J. Burggraaf, "High oxygen ion conduction in sintered oxides of the Bi₂O₃-Dy₂O₃ system," *J. Electrochemical Soc.*, **128** 75–82 (1981).
- H. Iwahara, T. Esaka, T. Sato, and T. Takahashi, "Formation of high oxide ion conductive phases in the sintered oxides of the system Bi₂O₃-Ln₂O₃ (Ln = La or Yb)," *J. Solid State Chem.*, **39** [2] 173–180 (1981).;
- T. Takahashi, T. Esaka, and H. Iwahara, "Conduction in Bi₂O₃-based oxide ion conductors under low oxygen pressure. I. Current blackening of the Bi₂O₃-Y₂O₃ electrolyte," *J. Appl. Electrochem.*, **7** [4] 299–302 (1977).

-
- ^{lxxxiii} T. Takahashi, T. Esaka, and H. Iwahara, "Conduction in Bi₂O₃-based oxide ion conductors under low oxygen pressure. I. Current blackening of the Bi₂O₃-Y₂O₃ electrolyte," *J. Appl. Electrochem.*, **7** [4] 299–302 (1977).
- ^{lxxxiv} K. Huang, J. Wan, and J.B. Goodenough, "Oxide-ion conducting ceramics for solid oxide fuel cells," *J. Mater. Sci.*, **36** [5] 1093–1098 (2001).
- H. Yahiro, Y. Baba, K. Eguchi, and H. Arai, "High Temperature Fuel Cell with Ceria-Yttria Solid Electrolyte," *J. Electrochem. Soc.*, **135** [8] 2077–2080 (1988).
- ^{lxxxv} A. V Virkar, "Theoretical Analysis of Solid Oxide Fuel Cells with Two-Layer, Composite Electrolytes: Electrolyte Stability," *J. Electrochem. Soc.*, **138** [5] 1481–1487 (1991).
- E.D. Wachsman, P. Jayaweera, N. Jiang, D.M. Lowe, and B.G. Pound, "Stable High Conductivity Ceria/Bismuth Oxide Bilayered Electrolytes," *J. Electrochem. Soc.*, **144** [1] 233–236 (1997).
- ^{lxxxvi} C. Oncel and Mehmet Ali Gulgun, "Interface Reactions Between the Anode and Lanthanum Gallate-type Electrolyte in Solid Oxide Fuel Cells," to be submitted to *J. Euro. Ceram Soc.*, March 2018.
- ^{lxxxvii} W. Zhu, Changrong Xia, Dong Ding, Xiaoya Shi, Guangyao Meng, Electrical properties of ceria-carbonate composite electrolytes. *Materials Research Bulletin*, **41**(11), p. 2057-2064 (2006).
- X. Wang, Ying Ma, Rizwan Raza, Mamoun Muhammed, Bin Zhu, Novel core-shell SDC/amorphous Na₂CO₃ nanocomposite electrolyte for low-temperature SOFCs. *Electrochemistry Communications*, 2008. **10**(10), p. 1617-1620 (2008).
- M. Benamiraa, A. Ringuedea, V. Albina, R.-N. Vannierc, L. Hildebrandtb, C. Lagergrenb, M. Cassir Gadolinia-doped ceria mixed with alkali carbonates for solid oxide fuel cell applications: I. A thermal, structural and morphological insight. *Journal of Power Sources*, 2011. **196**(13), p. 5546-5554 (2011).
- Z. Tang, Qizhao Lin, Bengt-Erik Mellander, Bin Zhu, SDC–LiNa carbonate composite and nanocomposite electrolytes. *International Journal of Hydrogen Energy*, 2010. **35**(7), p. 2970-2975 (2010).
- Z. Gao, Zongqiang Mao, Cheng Wang, Jianbing Huang and Zhixiang Liu, Composite electrolyte based on nanostructured Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) for low-temperature solid oxide fuel cells, *Int. J. Energy Res.* 2009; **33** (13), P. 1138–1144 (2009).
- G. Abbas, Rizwan Raza, M. Ashraf Ch. B. Zhu, Preparation and Characterization of Nanocomposite Calcium Doped Ceria Electrolyte With Alkali Carbonates (NK-CDC) for SOFC, *J. Fuel Cell Sci. Technol.* **8** (4), Research Papers, p. 041013 (2011).
- ^{lxxxviii} B. Zhu, Functional ceria–salt-composite materials for advanced ITSOFC applications. *Journal of Power Sources*, 2003. **114**(1), p. 1-9.
- B. Zhu, Next generation fuel cell R&D. *Int J Energy Res.* 2006, **30** (11), p. 895–903 (2006)
- Q.X. Fu, G.Y. Meng, B. Zhu, Intermediate temperature fuel cell based on doped ceria-LiCl-SrCl₂ composite electrolyte, *Journal of Power Sources*, 2002. **104** (1), p. 73-78 (2002).
- ^{lxxxix} S. Shawuti, C. Oncel, and M. A. Gulgun, "Solid Oxide-Molten Carbonate Nanocomposite Fuel Cells: I.", Particle Size Effect., *Journal of Power Sources*, **267**, pp 128-135, 2014.