Carbon-based Fuel Cell
Final Report
June 1, 2003 – July 30, 2005

Steven S. C. Chuang

February 12, 2006

Department of Chemical Engineering, The University of Akron

200 East Buchtel Commons

Akron, OH, 44325-3906

Phone number: 330-972-6993; Fax number: 330-972-5856

E-mail: schuang@uakron.edu

DE-PS26-03NT41803

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

The direct use of coal in the solid oxide fuel cell to generate electricity is an innovative concept for power generation. The C-fuel cell (carbon-based fuel cell) could offer significant advantages: (i) minimization of NO_x emissions due to its operating temperature range of 700 – 1000 °C, (ii) high overall efficiency because of the direct conversion of coal to CO₂, and (iii) the production of a nearly pure CO₂ exhaust stream for the direct CO₂ sequestration. The objective of this project is to determine the technical feasibility of using a highly active anode catalyst in a solid oxide fuel for the direct electrochemical oxidation of coal to produce electricity. Results of this study showed that the electric power generation from Ohio No 5 coal (Lower Kittanning) Seam, Mahoning County, is higher than those of coal gas and pure methane on a solid oxide fuel cell assembly with a promoted metal anode catalyst at 950 °C. Further study is needed to test the long term activity, selectivity, and stability of anode catalysts.

TABLE OF CONTENTS

ABSTRACT.....	3
LIST(S) OF GRAPHICAL MATERIALS.....	5
INTRODCUTION.....	6
EXECUTIVE SUMMARY.....	7
EXPERIMENTAL.....	9
RESULTS AND DISCUSSION.....	12
CONCLUSIONS.....	18
REFERENCES.....	18
LIST OF ACRONYMS AND ABBREVIATIONS.....	20

LIST(S) OF GRAPHICAL MATERIALS

Figure 1. The relationship between fuel processing and fuel cells.....	8
Figure 2. I-V curves of a YSZ fuel cell.....	12
Figure 3. I-V for petroleum coke and fuel mixtures for a Ni-based anode SOFC at 900 °C...	15
Figure 4. I-V for petroleum coke and fuel mixtures for a Ni-based anode SOFC at 950 °C...	16
Figure 5. IV of a SDC fuel cell.....	17

INTRODUCTION

Fuel cell is a device which allows the direct conversion of fuel to electric power. Solid oxide fuel cell (SOFC) holds a great promise for electric power generation due to its more flexibility in fuel usage than PEM fuel cell. The current solid oxide fuel cell system involves (i) use of natural gas or diesel fuel as a feed to a reformer for the production of syngas (a mixture of CO and H₂), (ii) cleaning of syngas, and (iii) the injection of syngas to the SOFC for the generation of the DC electricity.

The basic principle of the operation of the SOFC using syngas as the feed involves (i) a cathodic reaction: $O_2 + 2e^- \rightarrow O^{2-}$; (ii) the diffusion of the O^{2-} from the cathode to the anode through a solid electrolyte; and the anodic reaction (i.e., the electrochemical oxidation of CO and H₂) to produce electricity. The electrochemical oxidation of CO and H₂ can be written as follows:

The general requirement for generating electricity on the anode is the electrochemical oxidation of a fuel. This project was intended to determine the feasibility of developing an effective catalyst for catalyzing the electrochemical oxidation reaction of a solid carbon fuel. The reaction is written as below.

The development of a fuel cell which can directly utilize solid carbon could provide a number of significant advantages in the fuel cell system for the electric power generation. These advantages include the direct use of coal as the fuel and simplifying the fuel cell system by eliminating the fuel reforming steps.

EXECUTIVE SUMMARY

The objective of this phase I innovative project is to determine the technical feasibility of using coal as the fuel for a solid oxide fuel cell. This type of C-fuel cell (carbon-based fuel cell) could offer significant advantages: (i) minimization of NO_x emission due to the operating temperature range of 700 - 1000 °C, (ii) high overall efficiency because of the direct conversion of carbon to CO_2 , (iii) low investment and maintenance cost due to simplicity of the process, and (iv) easy of CO_2 sequestration due to the production of 99% purity of CO_2 .^{1,2}

Coal contains solid carbon, a variety of volatile hydrocarbons, heavy metals, metal oxides, and sulfur compounds. The key issue addressed in this project is whether the direct contact between the solid coal particle and the anode catalyst surface could lead to the direct electrochemical oxidation of carbon in the content of the coal particles.

Approach

- Develop an anode catalyst to promote the electrochemical oxidation of coal.
 - Use a cold-pressing technique to fabricate the electrolyte thin film.
 - Use a screen-printing technique to attach a cathode and an anode on the electrolyte.
- Use mass spectroscopy and infrared spectroscopy to monitor the composition of the effluents from the fuel cell.
- Measure the current and voltage output.
- Characterize the electrolyte, cathode, and anode materials with X-ray diffraction.

Accomplishments

- Design and construction of a solid oxide fuel cell which produced 100 mA/cm^2 at 0.6 V using Ohio#5 coal as the fuel.
- Successful test of the solid oxide fuel cell for the direct oxidation of methane.
- Test of the solid oxide fuel cell using hydrogen, methane, heptane, activated carbon, petroleum coke, and Ohio # 5 coal as fuels.
- Successful fabrication of intermediate temperature SOFC using SDC (i.e., Samarium-doped Ceria ($\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$)) as the electrolyte and SSC (i.e., Strontium-doped Samarium Cobaltite ($\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$)) as the cathode.
- The fuel cell using Pt as the anode, SDC as the electrolyte, and SSC as the cathode produced 100 mA/cm^2 at 0.4 V using H_2 as the fuel at 700 °C; 200 mA/cm^2 at 0.6 V at 800 °C.

Although the initial work for this study showed that the direct contact between the pulverized coal particle and the anode catalyst surface led to generation of the electricity and CO_2 , no long term study on the anode catalyst activity, selectivity, and deactivation characteristics has been done due to the batch operation mode of the laboratory scale fuel cell. The major challenges in this research include the fabrication of the anode-supported fuel cell and sealing of the fuel cell reactor. Difference in thermal expansion coefficients of the various catalyst and electrolyte components usually leads to the cracking of the fuel cell during thermal cycling. Further improvement is needed on the fabrication approaches for the fuel cell and refinement of the

anode catalyst structure and composition. The successful development of this proposed technology could eliminate the use of coal-fired boilers for power generation.³

The significance of this proposed direct coal fuel cell technology can be further illustrated by Figure 1 which summarizes the relationship between the fuel types and currently available fuel cell technologies. Although the low-temperature fuel cells (PEMFC and PAFC) perform well with H₂ fuel inputs, the need to generate highly purified H₂ from various feedstocks such as natural gas and coal brings major equipment complexities into the fuel cell systems, resulting in overall efficiency loss and significant cost penalties.^{4,5} The direct coal (i.e., carbon) SOFC technology will allow the direct use of coal without complications from the operation of coal gasification, water-gas shift, and selective CO oxidation reactors. The proposed direct carbon – based fuel cell technology could lead to a low cost approach for generation of electricity from coal with high purity CO₂ as a byproduct.

Figure 1. The relationship between fuel processing and fuel cells

Ref: N.F. Brandon, S. Skinner, B.C.H. Steele, *Annu. Rev. Mater. Res.* **2003**, 33:183-213

EXPERIMENTAL

High temperature YSZ electrolyte fuel cell

A solid oxide fuel cell system with a LSM/YSZ/Metal disk was set up. LSM ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) was prepared by a solgel process involving dissolving metal salts in an ammonium-EDTA solution.⁶ The YSZ solid electrolyte disc was custom-manufactured from TOSOH Corporation using 8% dense YSZ powder. The anode catalyst was prepared by impregnating aqueous solution of metal nitrates onto porous YSZ fibers obtained from Zircar Inc. The reaction temperature required for the electrochemical oxidation of coal to take place thereby defines the minimum operating temperature of the C-fuel cell.

Fabrication of SDC electrolytes and SSC cathodes intermediate temperature SOFCs

Since the YSZ fuel cell has to operate above 850 °C to obtain a sufficient power density, an extensive effort was devoted toward fabricating intermediate temperature (~600-800 °C) solid oxide fuel cells using samarium-doped ceria (i.e., SDC) electrolytes with a 20 % mol samarium dopant content ($\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$) and strontium-doped samarium cobaltite (i.e., SSC, $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$) electrodes.

SDC powders were prepared with nitrate reagents according to the pechini method. Cerium nitrate 99.5%, samarium nitrate 99.9%, ethylene glycol 99 + % and citric acid monohydrate ACS 99.0 % were purchased from Alfa Aesar and used without further purification. Stoichiometric amounts of each metal nitrate were weighted and dissolved in water at room temperature. The resulting material was mixed with a solution of citric acid and ethylene glycol (1.88 molar metal to citric acid ratio), and was allowed to undergo three consecutive steps: polymerization, solvent removal, and calcination.

In a typical SDC synthesis, 3.09 g of cerium nitrate and 0.79 g of samarium nitrate were weighted and dissolved in deionized water at room temperature. In a separate beaker, 5.86 g of a solution containing citric acid and ethylene glycol (60 % wt citric acid) was prepared. The above two solutions were then mixed under vigorous stirring at 70 °C. The resulting mixture was further heated to 90 °C and was allowed to react for several hours until yielding a yellowish foam. The obtained foam was removed from the beaker, placed in an alumina crucible, and calcined at 450 °C for 5 h at a heating rate of 5 °C/min. Finally, the material was crushed using a hand and pestle mortar to obtain a fine cream colored powder. The resulting SDC powder was dried milled for 24 h using a rotary ball milling device using a plastic container with ceramic grinding balls. The obtained material was dried for 2 hr at 120 °C, passed through a #120 sieve (125 µm size), and then calcined at 900 °C for 6 hr at a heating rate of 5 °C /min.

SSC ($\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$) powders were prepared using oxide reagents. Samarium (III) oxide 99.9%, cobalt oxide (II, III) 99%, and strontium carbonate 99.99% were purchased from Alfa Aesar and were used without further purification. Typical SSC synthesis involves use of 2.32 g of samarium oxide, 3.20 g of cobalt oxide and 0.98 g of strontium carbonate mixed in methanol. The resulting mixture was wet ball milled for 24 h using a plastic container and ceramic grinding balls. The obtained material was dried for 2 hr at 120 °C and then calcined at 800 °C for 6 hr at a heating rate of 5 °C /min.

The fuel cell materials were further processed by adding a PVB (Poly Vinyl Butyral) based organic binder and a number of additives including dispersant and solvent in order to enhance the strength of the ceramic green body. The amounts of additives such as binder, a dispersant, and a mixture of solvents were varied to obtain an optimum green body. In a typical green body preparation, 2.0 g of the fuel cell starting material (SDC or SSC) were weighted and

added to a solution containing a dispersant and a solvent at room temperature. The obtained slurry was subsequently grinded (wet milling) in a 3 lb laboratory ball mill containing zirconia balls for 7 h. The resulting material was further mixed with binder and solvent and grinded for three more hours. The resulting slurry was dried at room temperature for 2 h and finally re crushed using a hand and pestle mortar in to a fine powder form. The SDC was cold pressed in the form of a thin disc and calcined at 1500 °C. The sintered SDC disc was screen-printed with SSC as a cathode and an oxide material as anode.

Both current and voltage output data from the fuel cell were acquired by a PC with an interface and Labview™ software. The gaseous product was analyzed by a SRI 8610C gas chromatograph and a Pfeiffer QMS 200 mass spectrometer. The analysis of gaseous products, such as CO and CO₂, allows the determination of the fuel conversion efficiency and byproduct formation.

RESULTS AND DISCUSSION

Fig. 2 shows the performance (I-V curves) of a YSZ fuel cell with LSM as a cathode and a transition metal as an anode using pure CH₄ and Ohio No. 5 coal (Table 1) as fuels. Pulverized coal was loaded in the fuel cell reactor

Figure 2. I-V curves of a YSZ fuel cell

tube and was gradually heated to 950 °C. The C- fuel cell at 950 °C produced higher current density than that for the CH₄-fuel cell. It is remarkable to observe that the current-voltage (I-V) curve for coal is higher than that for methane. Comparison of CH₄ I-V curve in Fig. 2 with those in literature (7-15) shows that the current density for CH₄ is about 35% of the best reported data for the direct methane SOFC. This is due to the use of thicker solid YSZ electrolyte (i.e, 1 mm in thickness) in our fuel cell as compared with 50 μm in the literature.

Table 1 Ohio coal no. 5 (PSOC-1517)

PROXIMATE ANALYSIS				ULTIMATE ANALYSIS	
% Moisture as received		4.15		% Carbon	83.99
Dry % ash		4.80		% Hydrogen	5.50
Dry % volatile matter		37.98		% Nitrogen	1.88
Dry % fixed carbon		57.22		% Oxygen	8.63
SULFUR FORMS				CALORIFIC VALUE (BTU/lb)	14258
% Pyritic	0.70	% Organic	1.21	EQUILIBIRUM MOISTURE (%)	7.98
% Sulfate	0.01	% Total	1.92		

The analysis of the gaseous stream showed that the major product produced from the coal fuel cell is CO_2 with less than 5% of CO. CO concentration can be further decreased by decreasing the flow rate of Ar which was used to bring out the gaseous product for the analysis. SO_2 was only observed during heating of coal. SO_2 , CO, H_2 and CH_4 begin to form at 400°C . The concentration of SO_2 in the fuel cell effluent reached a peak at 650°C and then declined with temperature. As the temperature reached 750°C , the concentration of SO_2 in the fuel cell effluent decreased to zero, indicating that most of the organic sulfur has left the coal in the fuel cell. It is important to note that coal undergoes devolatilization as it is exposed to temperatures above 400°C . Under the operating temperature (i.e., $600 - 950^\circ\text{C}$) of the SOFC, coal is in the form of coke.

Fly ash produced from coal did not strongly adhere onto the anode catalyst surface. This observation is indeed remarkable, considering that the fly ash deposition and slagging are major concerns in the design of coal-fired boilers. Examination of the physical properties of the fly ash and its formation history revealed that the reason for fly ash not fusing on the anode catalyst surface could be that our fuel cell operation temperature is lower than the fly ash fusibility temperature.³ Analysis of fly ash by Galbraith laboratory showed that no sulfur was present in the fly ash. Repeated runs for more than 2 hours at 950°C on the same fuel cell gave the same level of electric power as that in the first run.

The high efficiency of carbon or coal fuel cells has been pointed out by Cooper who has performed thermodynamic analysis.¹ Results of the analysis of a pilot carbon fuel cell plant in Table 2 showed that the carbon fuel cell has a highest total efficiency because of the favorable thermodynamics of the carbon-oxygen reaction. It is important to note that the theoretical limit of carbon fuel is greater than one because ΔG for carbon oxidation is greater than ΔH . The high

value of ΔG (i.e., $\Delta G(T) = \Delta H - T\Delta S$) can be attributed to the reaction of solid carbon with oxygen to produce gaseous CO_2 and H_2O . The reaction involved with solid carbon contributes to ΔG through a significant increase in ΔS . This is in contrast to CH_4 and H_2 fuel cell reactions which involve gaseous reactant and gaseous product, giving little change in ΔS .

Cooper further pointed out that the chemical potential for the carbon is constant and independent of the extent of its conversion or position within the fuel cell because the reactant carbon and product CO_2 exist as pure substances in separate phases.² In principle, this allows all the carbon fuel to be completely consumed in a single pass. The above analysis and our results show that the direct use of coal as a fuel for the solid oxide fuel cell is both theoretically and technically feasible for power generation.

Table 2 Efficiency of solid oxide fuel cell

Fuel	Theoretical $=\Delta G^\circ(T)/\Delta H^\circ(T)\text{std}$	Limit	Utilization Efficiency, μ	$V(i)/V(i=0)$ $= \varepsilon v$	Actual $=(\Delta G/\Delta H^\circ\text{std})(\mu)(\varepsilon v)$	Efficiency
C	1.003		1.0	0.8	0.8	
CH_4	0.895		0.8	0.8	0.57	
H_2	0.70		0.8	0.8	0.45	

Efficiency of a fuel cell or battery is defined :
 = (Electrical energy out) / (Heat of combustion (HHV) of fuels input)
 = [Theoretical efficiency G/H][Utilization fraction μ][Voltage efficiency εv]
 = $[\Delta G(T)/\Delta H^\circ][\mu][V/V^\circ] = [\mu][nFV]/\Delta H^\circ$
 -- where $\Delta G(T) = -nFV^\circ = \Delta H - T\Delta S$

To further confirm the feasibility of the use of solid fuel and the requirement of sulfur resistance, we have prepared a Ni-based anode catalyst by impregnation of YSZ fibers (Zircar) and YSZ powder (Tosoh) in 7:3 ratio with $\text{Ni}(\text{NO}_3)_2$ and a transition metal precursor. The transition metal was added onto the Ni-anode to enhance its resistance to sulfur poisoning and coking. The Ni-based anode material was pasted on the anode side of YSZ disc (1 mm) using

glycerine and calcined at 1000°C for 4 hours. The cathode material was prepared by mixing Lanthanum Strontium Manganese Oxide (LSM) and YSZ powder in 1:1 ratio.

Figure 3. I-V for petroleum coke and fuel mixtures for a Ni-based anode SOFC at 900 °C

increased in the order: coke < coke/CH₄ < coke/H₂/H₂S < coke/CH₄/C₇H₁₆. The low open circuit voltage and the large decrease in the I-V curve at the low current density region suggest a significant activation polarization for petroleum coke as compared with other fuel mixtures.

Increasing the temperature to 950 °C led to a further increase in the current density (Fig. 4). It is interesting to observe that all the I-V curves were merged together, giving the same slope. These results suggest that the Ohmic resistance is dominated in these fuel cell operations and all the fuel and fuel mixtures gave the same level of activation polarization. The Ohmic resistance primarily resulted from the resistance of O²⁻ conduction over the electrolyte.

Fig. 3 shows the I-V curves of a Ni-based anode SOFC taken at 900 °C using petroleum coke provided by FirstEnergy at Akron. The petroleum coke consists of 81% carbon, 3% hydrogen, 1% nitrogen, 4.6 % sulfur, 0.2% ash, 10% moisture, 330 ppm Ni, 84 ppm Fe, and less than 2000 ppm Vanadium. The current density at 900 °C

Figure 4. I-V for petroleum coke and fuel mixtures for a Ni-based anode SOFC at 950 °C

Decreasing the thickness of the electrolyte could lead to a significant improvement of the current density by increasing O²⁻ flux. An alternative to enhance the O²⁻ flux is to search for a fluorite oxide electrolyte with low temperature and high oxygen anion conductivity.

It is interesting to note that H₂S did not lead to any

deactivation of the anode Ni-based catalyst. The failure of H₂S to poison the anode is due to the presence of a transition metal oxide which is known to impart its sulfur resistance to the Ni catalyst in the petroleum refining process.¹⁶

Figure 5. IV of a SDC fuel cell

SDC was selected as a potential electrolyte for the carbon fuel cell due to its high oxygen anion conductivity at low temperature. Figure 5 show the I-V curve of a SDC fuel cell using SSC as cathode and Pt metal as an anode with flowing a mixture of 12.5 cc/min of He and 12.5 cc/

min of H₂ saturated at room temperature with H₂O (3% volume H₂O). Comparison of SDC with YSZ fuel cell in electricity output suggests that the use of SDC electrolyte may lead to an enhancement of the current density of the direct carbon fuel cell.

CONCLUSIONS

The key observations and results obtained from Phase I research are summarized below:

- The activity of the metal/metal oxide anode catalysts for catalyzing the electrochemical oxidation of coal, petroleum coke, CH₄, and heptane depends on the composition of the anode catalyst
- A promoted Ni-based anode catalyst exhibits sulfur resistance and a good activity for electrochemical oxidation of heptane and H₂S.
- Fly ash produced from coal did not strongly adhere onto the anode catalyst surface.
- SDC could serve as an electrolyte to enhance the current density of the carbon-fuel cell.

The key issues to be addressed prior to scale up include (i) enhancement of power density and (ii) removal of fly ash. The former requires identification of the lead anode catalyst, optimization of the catalyst compositions and structure, and enhancement of O²⁻ diffusion rate across the solid electrolyte. Removal of fly ash calls for an ingenious design of the fuel cell reactor system.

REFERENCES

- 1 J. Cooper, Lawrence Livermore National Laboratory, Livermore CA, 2003, http://www.llnl.gov/str/June01/pdfs/06_01.1.pdf
- 2 J. F. Cooper, International Conference on Fuel Cell Science, Engineering and Technology, 2004.
- 3 'STEAM in generation and use', A Handbook of Babcock & Wilcox, 40th Edition, 1992.
- 4 A. Hamnett and P. Christensen, in 'Electrochemical and Photoelectrochemical Energy Conversion', ed. N. Hall, Cambridge, 2000.
- 5 A. J. Appleby and F. R. Foulkes, 'Fuel Cell Handbook', Van Nostrand Reinhold, 1989.
- 6 Y. H. Huang, "Soft Chemical Synthesis and Transport properties of La_{0.7}Sr_{0.3}MnO₃ Granular Perovskites" *Solid State Communications*, 2000, **114**, 43.

7. S. A. Barnett, in 'Direct hydrocarbon SOFCs', ed. W. Vielstich, H. A. Gasteiger, and A. Lamm, New York, 2003.
8. R. J. Gorte, S. Park, J. M. Vohs, and C. Wang, "Anodes for direct oxidation of dry hydrocarbons in a solid-oxide fuel cell" *Advanced Materials (Weinheim, Germany)*, 2000, **12**, 1465.
9. R. J. Gorte and J. M. Vohs, "Novel SOFC anodes for the direct electrochemical oxidation of hydrocarbons" *Journal of Catalysis*, 2003, **216**, 477.
10. T. Hibino, A. Hashimoto, M. Suzuki, and M. Sano, "A solid oxide fuel cell using Y-doped BaCeO₃ with Pd-loaded FeO anode and Ba_{0.5}Pr_{0.5}CoO₃ cathode at low temperatures" *Journal of the Electrochemical Society*, 2002, **149**, A1503.
11. T. Hibino, A. Hashimoto, M. Yano, M. Suzuki, S.-I. Yoshida, and M. Sano, "High performance anodes for SOFCs operating in methane-air mixture at reduced temperatures" *Journal of the Electrochemical Society*, 2002, **149**, A133.
12. T. Hibino, T. Hashimoto, T. Inoue, J.-I. Tokuno, S.-I. Yoshida, and M. Sano, "A low-operating-temperature solid oxide fuel cell in hydrocarbon-air mixtures" *Science (Washington, D. C.)*, 2000, **288**, 2031.
13. B. C. H. Steele, "Appraisal of Ce_{1-y}Gd_yO_{2-y/2} electrolytes for IT-SOFC operation at 500 DegC" *Solid State Ionics*, 2000, **129**, 95.
14. B. C. H. Steele, P. H. Middleton, and R. A. Rudkin, "Material science aspects of SOFC technology with special reference to anode development" *Solid State Ionics*, 1990, **40-41**, 388.
15. S. A. Barnett, 'Handbook of Fuel Cells', ed. A. L. W. Vielstich, H. A. Gasteiger, Wiley, 2003.
16. B. C. Gates, 'Catalytic Chemistry', Wiley, 1992.

LIST OF ACRONYMS AND ABBREVIATIONS

C-fuel cell: carbon-based fuel cell

SOFC: solid oxide fuel cell

SDC: Samarium-doped Ceria ($\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$)

SSC: Strontium-doped Samarium Cobaltite ($\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$)

YSZ: Yttria-stabilized zirconia

LSM: $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$