Experimental Study of Self-Sustained Electrochemical Promotion Catalysts for Heavy Hydrocarbon Reforming

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EXPERIMENTAL STUDY OF SELF-SUSTAINED ELECTROCHEMICAL PROMOTION CATALYSTS FOR HEAVY HYDROCARBON REFORMING

By

Zedong Wang

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Hydrogen production from reforming bio-fuels is considered as one of the major ways of utilizing renewable energy sources. Conventionally, most reforming catalysts are noble metal catalysts with high operation temperature above 1000 °C, which result in low thermal efficiency, long start-up time and use of high grade materials. These reasons hinder the development of hydrogen production technology.

Novel self-sustained electrochemical promotion (SSEP) catalysts were developed and evaluated for heavy hydrocarbon reforming at relatively low temperatures, 450 to 650 °C. Typically, the SSEP catalysts contain NiO/Ni/CuO/Cu/\( \text{CeO}_2 \) as a selective anodic phase, \( \text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3 \) (LSM) as a selective cathodic phase, yttria stabilized zirconia (YSZ) as an oxygen ion...
conduction phase, and Ni/Cu also as an electronic conduction phase. The reforming performance of the SSEP catalysts was evaluated using a fixed bed reforming reactor for n-pentadecane. A commercially available noble metal containing catalyst, 2.4 %Pt on CeO$_2$ support, was evaluated using exactly the same method.

The following conclusions can be drawn as a consequence of this study:

1) The fuel conversion for the SSEP catalyst was 10 folds of that for the noble metal catalyst and the yield of hydrogen and carbon monoxide for the SSEP catalysts was 100 folds of that for the noble metal catalyst at 450°C.

2) The experimental results prove that this unprecedented result for the SSEP catalysts is due to the coupling of four constituent components of the SSEP catalysts, specifically, transport of oxygen ions through the oxygen ion conduction phase and transport of electrons through the electronic conduction phase between the selective anodic phase and the selective cathodic phase. This coupling gives rise to positive electrochemical potential shifting on the anode and thereby electrochemical promotion.

3) The study of the effect of each component and the effect of the concentration clearly reveals that the performance of the SSEP catalysts can be further
improved to a higher level by the following ways: i) replacing the solid electrolyte, YSZ with one that has a higher oxygen ion conductivity than that of YSZ at lower temperatures; ii) replacing the cathode material, LSM with one that has a higher cathodic activity; iii) selectively depositing the anode only on the surface of the YSZ. These further verify the SSEP mechanism for the catalytic reforming process.

In addition, all the catalysts were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Transmission Electron Microscopy (TEM) and Accelerated Surface Area and Porosimetry Analyzer 2020 (ASAP 2020).

All solid state electrochemical sensors were also prepared. The experiments results demonstrate that the feasibility of the solid state electrochemical sensor. The new solid state electrochemical sensor is sensitive and reliable for the surface quality control.
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AFM - Atomic force microscopy
ATR - Auto-thermal reforming
BET - Brunauer Emmett Teller
CPE - constant phase element
CPOXR - Catalytic partial oxidation reforming
CV - Cyclic voltammetry
DL - Double layer
ECS - Electrochemical sensor
EDAX/EDS - Energy dispersive x-ray spectroscopy
E_F - Fermi level
EIS - Electrochemical impedance spectroscopy
EP - Electrochemical promotion
EPR - Equivalent parallel resistance
ESR - Equivalent series resistance
FCV - Fuel cell vehicle
FTIR - Fourier transform infrared spectroscopy
GC - Gas chromograph
GDC - Gadolinium doped ceria
GLNCe - GDC, LSM, Ni, Cu, CeO_2
GLNZCCe - GDC, LSM, Ni, Zn, Cu, CeO_2
ICE - Internal combustion engine
ICP - In situ controlled promotion
LNCCe - LSM, Ni, Cu, CeO_2
LSCF - La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3
LSCo - Lanthanum strontium cobaltite
LSM - Lanthanum strontium manganese oxide, La_{0.9}Sr_{0.1}MnO_3
MIEC - Mixed ionic electronic conductors
NDI - Non-destructive inspection
NDT - Non-destructive testing
NEMCA - Non-faradaic electrochemical modification of catalytic activity
PEM - Proton exchange membrane (fuel cell)
PMMA - Polymethyl methacrylate
POX - Partial oxidation
POXR - Partial oxidation reforming
PSA - Pressure adsorption
PTFE - Polytetrafluoroethylene
SC-SOFC - Single-chamber solid oxide fuel cell
SEM - Scanning electron microscopy
SIMS - Secondary ion mass spectroscopy
SOP - Standard operation procedures
SR - Steam reforming
SSCo - Samarium strontium cobaltite
SSEP - Self-sustained electrochemical promotion
TEM - Tunneling electron microscopy
TPB - Three-phase-boundary
XPS - X-ray photon spectroscopy
XRD - X-ray diffraction
YSZ - Yttria stabilized zirconia, (Y$_2$O$_3$)$_{0.08}$(ZrO$_2$)$_{0.92}$
YLCCe - YSZ, LSM, Cu, CeO$_2$
YLFNCCe - YSZ, LSCF, Ni, Cu, CeO$_2$
YLNCCe - YSZ, LSM, Ni, Cu, CeO$_2$
YNCCe - YSZ, Ni, Cu, CeO$_2$
Φ - Work function
Ψ - Volta potential
CHAPTER 1 INTRODUCTION

In this chapter, firstly, the significance of the catalyst research is discussed. Secondly, a novel concept of self-sustained electrochemical promotion catalyst is presented, based on a critical review of conventional catalysts and the electrochemical promotion system. Thirdly, the possible benefits of this kind of novel catalyst and the objectives of the research are also presented. In addition, the research motives and objectives for the solid-state electrochemical sensor, and the organization of the dissertation are outlined.

1.1 Self-sustained electrochemical promotion (SSEP) catalysts at low temperatures

1.1.1 Significance of this research on development of fuel cell industry

Due to the relatively fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio of PEM fuel cells, they are becoming particularly suitable for use in passenger vehicles, such as cars and buses. However, a significant barrier to using these fuel cells in vehicles is hydrogen storage. Most fuel cell vehicles (FCVs) powered by pure hydrogen must store the hydrogen onboard as a
compressed gas in pressurized tanks. Due to the low-energy density of hydrogen, it is difficult to store enough hydrogen on-board to allow vehicles to travel the same distance as gasoline-powered vehicles before refueling, typically 300–400 miles. Higher-density liquid fuels, such as biodiesel, ethanol, natural gas, liquefied petroleum gas, and gasoline, can be used for fuel, but the vehicles must have an on-board fuel processor to convert the fuel into hydrogen.

![Figure 1.1. Schematic of the fuel cell car with on-board reformer.](image)

The fuel processor includes three parts: reformer, water-gas shifting, and cleaning. The reformer is the key part of the fuel processor. The performance of the processor highly depends on the performance of the reforming catalyst in the reformer. Currently, most of reforming catalysts are precious-metal catalysts and...
their effective temperature range is very high, above 1000 °C. The disadvantages of traditional reforming catalysts are obvious:

1. The performance of the catalyst can’t meet the design requirement of reformers.

As subsystems of fuel cell systems, the onboard reformers are required to have a specific power density of 2.25 kW/kg, energy efficiency of >80 %, fast response, and high durability (>5000 hrs).

2. Large amounts of catalyst is needed for timely fuel reforming; the large amount necessary to convert all the fuel, coupled with the high cost of precious metal catalyst, increases the total cost of the fuel cell car.

3. High operation temperatures lead to longer start-up times and low thermal efficiency.

Therefore, it is necessary to develop a high performance non-precious metal catalyst with low operation temperatures.

1.1.2 A critical review of conventional catalysts for CPOX

Common catalyst includes two parts: catalyst and catalyst support. The catalyst supports such as alumina provide a catalyst carrier that prevents sintering or ripening of the active phases to ensure a stable, high active surface area. Use of oxygen ion
conducting materials including ceria and zirconia as catalyst supports has been a focus of research because these supports enable so called metal-support interactions [1-5]. Catalysts on non-stoichiometric ceria exhibit much greater oxidation catalytic activity than catalysts on other supports. The main reason is that the ceria support provides surface oxygen species for the oxidation reaction and the consumed oxygen in the lattice is replaced via transfer of oxygen from oxidizing molecules to the lattice. Thus the catalyst support is not only a carrier, but also an oxygen ion supplier. However, for all these catalyst systems, the activity of the catalyst is only promoted at the vicinity of the three-phase boundary (TPB), a site only a few nanometers wide, as shown in Figure 1.2.
This conventional concept of catalyst design at the nanometer level has certain successes, but it does not satisfy the above requirements for reforming technology.

Figure 1.2. Hydrocarbon reforming reaction routes on a metal catalyst on alumina.

In the early 1980s, a non-Faradaic electrochemical modification of catalytic activity, or NEMCA, effect was discovered by Vayenas et al. [6-10] and the so-called electrochemical promotion process was soon developed. This process is based on controlling, by an applied potential, the work function of a working electrode via continuous supply of short-lived sacrificial promoters, such as $O_2^-$, $O_2^{2-}$, $O^-$, or most likely $O^{3-}$, which are produced continuously at a counter electrode and diffuse to the working electrode through a solid oxide electrolyte by surface paths.

The rate enhancement ratio, $\rho$, is defined by Equation 1.1 [11]. Also useful is the
enhancement factor (electrochemical promotion efficiency), \( \lambda \). This is defined by Equation 1.2.

\[
\rho = \frac{r}{r_0} \quad (1.1)
\]

\[
\lambda = \frac{(r - r_0)}{I} \frac{I}{2F} \quad (1.2)
\]

In these equations, \( r \) is the catalytic rate of promotion at current \( I \) that is provided by the external power sources, \( r_0 \) is the open-circuit catalytic rate, and \( F \) is Faraday’s constant.

According to Faradic theory, when the external power source is added to the catalyst system, the reaction rate should be equal to \( r_0 + \frac{I}{2F} \times 10^4 \) as shown in Figure 1.3.

The reaction rate for the half electrochemical reaction shown in Equation 1.3 is \( I/2F \).

\[
\text{C}_2\text{H}_4 + 6\text{O}^2^- \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + 12\text{e}^- \quad (1.3)
\]

However, the real catalytic oxidation reaction rate is much higher than this.

\[
\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (1.4)
\]

The current induced rate change for the catalytic reforming is shown in Equation 1.4, for cases where \( \Delta r \gg I/2F \). The reason is because as oxygen ions are continually
supplied to the metal catalyst, some of the oxygen ions backspillover to the surface of
the metal catalyst and form an effective double layer. That double layer is shown in

Figure 1.4.

Figure 1.3. Electrochemical promotion using an external power supply.

This changes the work function and the chemisorptive properties of the metal
catalyst. These backspillover oxygen ions are less reactive than the oxygen atoms
adsorbed from the gas phase. Thus, the lifetime of the oxygen ions is long enough as
sacrifice promoters for the reforming reaction. In the electrochemical promotion
catalyst system, the activity of the catalyst is promoted not only at the TPB, but also at the whole gas-exposed surface of the metal catalyst as shown in Figure 1.4.

![Figure 1.4. Mechanism of electrochemical promotion.](image)

It has been demonstrated that the electrochemical promotion efficiency for catalytic reforming can be more than 2 orders of magnitude better, such that \( \lambda >> 1 \), even at very low current densities such as \( \sim 1 \mu \text{A} \). Such a remarkable increase in reaction rate provides great potential for catalytic reforming.

The preceding review clearly reveals that the reforming reaction rate can be increased with the use of a catalyst. The performance of the catalyst can be improved by the following three ways:
1. To promote the activity of the catalyst at the three phase boundary via metal-support interactions. e.g. by depositing the catalyst on the right catalyst supports, the activity of the catalyst at the three phase boundary point (between catalyst support-metal and catalyst-gas reactants) is promoted [14-19].

2. To promote the activity of the catalyst at the whole exposed surface by depositing some promoters [21-23].

3. To combine these two promotion methods to promote the activity of the catalyst at the three phase boundary and the whole exposed surface by the NEMCA or electrochemical promotion.

   However, the electrochemical promotion could only be enabled using an external power source or a short-circuiting of the anode and cathode of an electrochemical cell, which is equivalent to a single-chamber solid oxide fuel cell (SC-SOFC) [11]. This is neither realistic nor easy to be realized.

1.1.3 SSEP catalysts and their benefits

   This thesis presents a new concept: self-sustained electrochemical promotion (SSEP) catalysts, which can take advantage of electrochemical promotion without use of an external power source. The basic concept is schematically illustrated in Figure
1.5. The SSEP catalysts consist of four main components: selective anodic catalysts, selective cathodic catalysts, $O^{2-}$ ion conductors, and electronic conductors.

![Diagram of electrochemically promoted partial oxidative reforming of fuel $C_mH_n$]

Unlike normal electrochemical promotion devices with separated anodes and cathodes, these catalysts contain tiny anodes and cathodes in the form of fine particles, typically ranging from 20 nm to 0.5 µm in size.

The electrochemical promotion does not need an external power supply, or, it is self-sustained. Because of the difference of the electrochemical potentials [12, 13] between the selective cathodes and anodes, the oxygen ion species, $O^{2-}$, is produced at the cathode and driven to the anode through the oxygen ion conductor to participate in the oxidation of the hydrocarbon, while the electrons produced from the oxidation...
reaction are driven to the cathode through the electronic conductor and participate in the reduction of oxygen.

Possible benefits of the SSEP catalyst are as follows:

1) Promotion due to the improvement from traditional “point catalysts” to “area catalysts.” For this new kind of catalyst, backspillover happens on the Ni and Cu. The backspillover of oxide ions O\(^{\delta^+}\) is accompanied by their compensating charge δ\(^+\) in the metal, thus forming backspillover dipoles and establishing an effective electrochemical double layer on the gas-exposed, catalytically active electrode surface. The equilibrium condition for reaction now can take place not only at the “point” three phase boundary, but over the entire gas exposed metal electrode surface, the “area.”

2) In the double layer, the field strength, $\hat{E}$, within the effective double layer is typically of the order of 1 V/Å or \(10^{10}\) V/m. This parameter, which equals $d\varphi/dz$ within the double layer, plays an important role in electrochemical promotion. This strong field strength can help the reactions break the reactant down into atoms, resulting in a promotion. A schematic is presented below; it attempts to show precisely how the double layer and the concomitant electric field facilitate the breaking down of
hydrocarbon molecules into more useful products such as gaseous hydrogen and methane.

3) The close proximities (distances of 20 nm to 20 µm) between anode and cathode phases allow efficient transportation (low IR drop) of electrons and oxygen ions and enable an effective coupling between the two half-cell electrochemical reactions.

4) In addition to the NEMCA effect, the coupling between anode and cathode phases at short or long distances increases the effective reaction cross-section to a much greater value than that for Al₂O₃ (an insulator) -supported catalysts. This coupling is equivalent to increasing the probability with which the reacting molecules meet at the active sites. In the case where a small area of anode is coupled with a large area of
cathode, as shown in Figure 1.7, the oxidation on the anode area can be further accelerated.

![Figure 1.7. SSEP Reduction of oxygen and partial oxidation of hydrocarbons.](image)

5) When there is a sufficient supply of oxygen or $O_2^{2-}$, carbon deposition can be mitigated. As illustrated in Figure 1.8, in which $O_2^{2-}$ is constantly supplied through the catalyst surface and subsurface lattice to the vicinity of the carbon deposit sites, where carbon oxidize more easily. The possible application of the SSEP catalysts is used as the paint for the environment [20].
The effect temperature of the SSEP catalyst can be as low as 350 °C. For example the nuclear reactor, the temperature can reach above 350 °C, under the environment with H₂ and O₂, the catalyst can promote the reaction to produce water.

![Diagram of carbon oxidation on SSEP catalysts]

Figure 1.8. Oxidation of carbon deposit on SSEP catalysts.

1.1.4 Objectives of the research on the reforming catalysts

Three major objectives of this study are: 1) to prove the concept of self-sustained electrochemical promotion catalysts by the experimental study; 2) to evaluate and clarify the effects of the concentrations of ingredient proportions in SSEP catalysts; 3) to demonstrate that the performance of the SSEP catalysts can be further improved by optimizing the composition and/or by using more effective materials that facilitate the electrochemical processes.
1.2 All solid state electrochemical sensor

1.2.1 Motivations

Continuous improvement of the strength and durability of bonded structures is the key to the overall acceptance of the processing and fabrication technologies in aerospace industry, especially in applications of the technologies in manufacturing primary aircraft structures [24]. The design principle for any adhesive-bonded joints or adhesive bonds requires that the cured adhesive be always stronger than the strength of the adherend [24]. Surface pretreatment or preparation has been implemented in aerospace industry for many years as a process to ensure strong adhesive bonds. Many of the pretreatment procedures result in adhesive bonds that have high initial bond strength but do not always demonstrate expected durability [25, 26]. Service experiences with adhesive-bonded joints have displayed variable strength and durability. Some provide extended service lives while others fail before their expected service lives. For example, adhesive bond failures were cited as the major cause for 53% of structural defects in the Royal Australian Air Force [24]. Analyses of the bond failures have revealed that many of the adhesive-bonded joints failed at the interface between adhesive and adherend (adhesion failure mode)
Such a wide variation in bond durability [25, 26, and 31-34] strongly suggests deficiencies in the quality control of the surface pre-treatment and bond fabrication processes and a lack of an in-field definitive surface inspection method.

Surface pretreatment prior to adhesive bonding is vital for achieving high bond strengths and bond durability for high-performance aerospace applications [26]. From a quality control viewpoint, the surface physical and chemical properties including the surface roughness, tension, composition, oxidation/reduction states or activity, and the thickness of the active layer should be uniform and easily reproducible. The main objective of a surface pretreatment procedure is to provide clean, fresh and active surfaces that permit formation of strong and durable bonds between the adherends and the applied adhesive. The pretreatment techniques can be classified according to the desired outcomes, such as removing surface contaminants and producing chemically activated surfaces for enhancing the bond strength and durability. Pretreatment methods can also be categorized according to the nature of the processes, such as peel ply, tear ply, mechanical abrasion, solvent degreasing/wiping, irradiation treatments (corona discharge, plasma, flame, and laser), wet chemical treatments (chemical etching, anodizing), surface coating
(sol-gel, plasma spray, sputtering), and primer application. Usually, an optimal pretreatment procedure for a specific adherend/adhesive system is a sequential combination of several pretreatment methods.

Most of the analytical surface chemistry characterization technologies are only suitable for laboratory studies but not for in-field inspections due to either lengthy sample preparation procedures, limitations to sample sizes, requirements for high vacuum, or limited sensitivity under realistic physical and chemical conditions. The analytical technologies include X-ray photon spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy disperse analysis of X-ray (SEM-EDAX), transmission electron microscopy (TEM), atomic force microscopy (AFM), and secondary ion mass spectroscopy (SIMS). A number of industrial non-destructive inspection (NDI) methods including conventional ultrasonic techniques, oblique incidence ultrasonic technique, Lamb waves, sonic vibrations, spectroscopic methods, acoustic emission, thermal methods, radiography, and optical holography, have been used to detect defects in adhesive bonded structures [24-26, 28, and 29]. While these NDI tests eliminate bonds with detectable defects and cracks, they are not capable of providing
assurance of bond strength and long-term durability. For instance, these NDI technologies cannot detect the so called “kissing bond” [35] or weak bonding due to weak intermolecular interactions at the interfaces between the adhesive and adherend molecules, because these interface defects may be as large as a few atoms and well below the sensitivity of the industrial NDI technologies. In fact, quality assurance for surface pretreatment and bonding processes in industries relies on implementation of standard operation procedures (SOP) for the adherend surface preparation and bonding procedures [26, 36]. However, because we lack an in-field definitive surface inspection method, laborious, sometimes inadequate, and sometimes excessive measures are used to ensure the quality of adhesive bonding, thereby creating an undue expense on an otherwise economic manufacturing process.

1.2.2 Objectives of research

The discovery of the mediated electrochemical cell and the availability of Nafion™ solid electrolyte provided an indelible opportunity to develop an all solid-state electrochemical sensor that can be used to detect the chemical properties or contaminations on a composite surface. It is thus of great interest to conduct a
feasibility study of a solid-state electrochemical sensor for in-field surface chemical analysis. Electrochemical analyses give us an idea of the surface oxidation situation.

1.3 Organization of the thesis

This dissertation is divided into 7 chapters, and includes two foci. Chapters 2 through 6 belong to the self-sustained electrochemical promotion catalysts. Chapter 7 mainly discusses the solid-state electrochemical sensor.

In Chapter 2 the necessary literature is reviewed, and the hydrogen economy and conventional hydrocarbon processing were reviewed first. Due to the advantages of partial oxidation reforming (POXR), the currently used catalyst for POXR was summarized. With these new catalysts, the reforming temperature for POXR can be decreased significantly.

In Chapter 3 the experimental section, different kinds of catalysts were synthesized. All these catalysts including the commercial catalyst were studied by their partial oxidation reforming performance. All the catalysts are investigated by SEM, EDS, XRD, TEM and BET specific surface area methods.

In Chapter 4, the scientific hypothesis of self-sustained electrochemical promotion (SSEP) catalysts is proved. Novel SSEP catalysts were developed and
evaluated using a fixed bed reforming reactor for n-pentadecane. The experimental results prove that the novel SSEP catalysts provide a new unprecedented approach for catalyst design that enables coupling of four or more different components.

In Chapter 5, the composition effect in the SSEP catalysts was evaluated. The experimental results prove that the entire set of components in the SSEP catalysts is necessary to reach the high performance. Most important are the components YSZ and LSM. Further, the effects of their concentrations in the SSEP catalyst are also investigated. From the POX reforming results and SEM, EDS, BET specific surface area analyses, it is clearly revealed that the performance of the SSEP is affected by the concentration of ingredients in the SSEP catalyst. These results predict that the performance of the SSEP may be limited by the properties of the component materials.

In Chapter 6, as discussed in Chapter 5, the performance of the SSEP catalyst YLNCCe is affected by the concentration and limited by certain properties of the materials. Thus, the possibility of improving of the SSEP catalyst lies in the ability to adopt new materials. In this chapter, two improved SSEP catalysts are studied. One is GLNCCe, which is made by using GDC to substitute the YSZ. The
performance of the GLNCCe is better than that of the YLNCCe. The POX reforming results combined with the SEM, EDS, XRD and BET specific surface area analyses prove the mathematic model of the SSEP catalysts in Chapter 4. The other way of possibly improving SSEP catalysts is by adopting new cathode materials like LSCF to substitute the LSM. The performance was determined to hinder more than help, however. Sources agree that the reason is mainly due to interactions between YSZ and LSCF that try to produce new materials, like in a chemical reaction, and this decreases the performance of the SSEP catalysts.

In Chapter 7, the solid-state electrochemical sensor was presented. In this chapter, the need for a non-invasive in-field detection sensor was also reviewed. The solid-state electrochemical sensor was developed for surface quality control, including surface moisture control and contaminant detection. The experimental results show that this kind of sensor is highly sensitive to moisture and contaminants on the materials surface.
CHAPTER 2 LITERATURE REVIEW

2.1 Applications of Hydrogen in Automobiles

Hydrocarbons have always been the most commonly used fuels. The combustion of hydrocarbons in an internal combustion engine (ICE) enables the conversion of the potential energy of the hydrocarbons into mechanical energy and then electrical energy. In general, the overall efficiency of this process ranges between 15 % and 25 %.

Proton exchange membrane fuel cells (PEMFC) are a promising alternative to the IC engine for automobiles, distributed power generation, and portable electronic devices. They exhibit an electrical efficiency of up to 60 %. A major barrier to using these fuel cells in automobile applications is hydrogen storage. Most fuel cell vehicles (FCVs) powered by pure hydrogen must store the hydrogen on-board as a compressed gas in pressurized tanks or cryogenic liquid hydrogen. Due to the low-energy density of hydrogen, it is difficult to store sufficient hydrogen on-board to allow vehicles to travel the same distance as gasoline-powered vehicles before refueling, typically 300–400 miles. Higher-density liquid fuels, such as biodiesel, ethanol, natural gas,
liquefied petroleum gas, and gasoline, can be used for fuel, but vehicles must have an on-board fuel processor to produce hydrogen from fuel. One of primary components of the fuel processor is a reformer that converts liquid hydrocarbons into \( \text{H}_2, \text{CO}, \text{CO}_2, \) and minor hydrocarbon gases. The performance can be increased by the optimization design [20].

2.1.1 Hydrogen economy

Hydrogen is the most abundant element on the earth and in the universe and is considered as a leading fuel candidate in the future. However, on the Earth the hydrogen has to be extracted primarily from fossil fuels or separated from water [38, 39]. Power sources (e.g. ICE and fuel cells) based on hydrogen from renewable resources, if implemented on a large scale, could improve energy security, air quality, and help control greenhouse gas emissions.

The global market of hydrogen is already greater than $40 billion per year [40]. The basis of hydrogen energy is that hydrogen reacts with oxygen to produce energy and water [41]. Hydrogen has a high gravimetric energy density of 122 kJ/g (kiloJoules per gram), which is 2.75 times greater than hydrocarbon fuels. When hydrogen and oxygen combine to form water, the following relations describe the
chemical reaction taking place (Equation 2.1), and the energy transformations that accompany such a change (Equations 2.2 - 2.3).

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad (2.1) \]

\[ \Delta H^\circ = -286 \frac{\text{kJ}}{\text{mol}} \quad \text{at 25 °C} \quad (2.2) \]

\[ \Delta G^\circ = -237.2 \frac{\text{kJ}}{\text{mol}} \quad \text{at 25 °C} \quad (2.3) \]

### 2.1.2 Conventional hydrocarbon processing

There are many ways to produce hydrogen, including via a reformation of fossil fuels and biomass, and electrolysis of water [42].

![Diagram](image)

Figure 2.1. The production process for converting a hydrocarbon fuel into H\textsubscript{2}.

Figure 2.1 shows a schematic of the process of reforming hydrocarbons from fossil fuels. Hydrogen production that relies on fossil fuels constitutes more than 95%
of global hydrogen production, as shown in Figure 2.2. Of the ways to reform hydrogen from gaseous and liquid hydrocarbon fuels, the three most commonly used are steam reforming (SR), partial oxidation reforming (POXR), and autothermal reforming (ATR) [43, 39].

![Figure 2.2. Global Hydrogen production share by source [7].](image)

1) Steam reforming

   Historically, steam reforming has been the most popular method of converting light hydrocarbons into hydrogen. The fuel is heated and vaporized, then injected with superheated steam into the reaction vessel. The steam-to-carbon molar ratio is usually in the neighborhood of 2.5:1 but developers strive for lower ratios to improve cycle efficiency.
The major governing equation describing the SR process is prescribed by Equation 2.4.

\[
C_xH_y + x H_2O \rightarrow x CO + (x + \frac{y}{2}) H_2
\]  

(2.4)

However, steam reforming is a highly endothermic process, so an external source of heat is needed. The operation temperature usually is 700 – 900 °C on Ni-based catalysts. The process suffers from some limitations making it extremely inefficient. These limitations include reversibility, diffusion limitation; carbon formation and a deactivation limit. Therefore, although steam reforming is a mature technology, its main drawbacks have yet to be overcome to improve the overall process for both large-scale production and micro fuel processing.

2) Partial oxidation reforming

More and more scientists are becoming interested in the catalytic partial oxidation reforming reaction, after the high yields in CO and H\(_2\) (also known as synthesis gases) were achieved by a reforming reaction at very short contact times (10\(^{-2}\)–10\(^{-4}\) s) without steam and/or CO\(_2\) [39, 49-51]. This leads to the introduction of compact catalytic partial oxidation reforming reactors. The partial oxidation of hydrocarbons occurs when a sub-stoichiometric amount of oxygen is supplied to the reaction thereby
causing partial combustion to occur [52, 53]. Similar to combustion, partial oxidation is also an exothermic reaction; however, the amount of heat released is considerably less than the heat release caused during complete combustion of the fuel. The general relation of the partial oxidation of hydrocarbons is as follows [44]:

\[
C_xH_y + (x/2)(O_2 + 3.76N_2) \rightarrow x\text{ CO} + (y/2)\text{H}_2 + (x/2)(3.76N_2)
\] (2.5)

Partial oxidation reactions are thought to proceed in two distinct phases: a rapid, highly exothermic combustion phase where all free oxygen is consumed to give off heat and form the products of CO\(_2\) and H\(_2\)O; and a much slower endothermic reforming phase where residual unconverted fuel reacts with the CO\(_2\) and H\(_2\)O plus the reaction heat to form syngas products H\(_2\) and CO [45-48].

3) Auto-thermal reforming

The coupling of SR with POX is termed autothermal reforming (ATR). Some define ATR as a SR reaction and a POX reaction that takes place over microscopic distances at the same catalytic site, avoiding complex heat exchange. Others have the less restrictive definition that ATR occurs when there is no wall between a combined SR reaction and catalytic POX reaction. ATR is carried out in the presence of a catalyst that controls the reaction pathways and thereby determines the relative
extents of the POX and SR reactions [54-56]. The SR reaction absorbs part of the heat generated by the POX reaction, limiting the maximum temperature in the reactor. The net result can be a slightly exothermic process. The net enthalpy change for the auto-thermal reforming is zero (\(\Delta H = 0\)).

\[
C_xH_y + n[O_2 + 3.76 \text{ N}_2 + (x - 2n)\text{H}_2\text{O}] \rightarrow x\text{CO} + (x - 2n + \frac{y}{2})\text{H}_2 + 3.7n\text{N}_2
\]

(2.6)

### 2.1.3 Key aspects to the reforming performance

1) Oxygen-to-carbon ratio

The oxygen-to-carbon (O/C) ratio is the ratio of twice the molar oxygen flow rate versus the molar flow rate of the fuel carbon within a hydrocarbon oxidation reaction scheme.

\[
\text{O/C ratio} = \frac{2nO_2}{xn_{C_xH_y}}
\]

(2.7)

It is an important parameter used to identify the regime of the hydrocarbon oxidation system (i.e. combustion versus partial oxidation regimes). e.g. O/C ratio of 1 denotes the stoichiometric partial oxidation point of a fuel conversion process where exactly one mole of carbon is combined with one mole of atomic oxygen to form CO.
2) Steam-to-carbon ratio

Similar to the O/C ratio, the steam-to-carbon ratio (S/C) is the ratio of the molar flow rate of H$_2$O to the molar flow rate of the fuel carbon:

$$S/C \text{ ratio} = \frac{2n_{H_2O}}{xn_{C_xH_y}}$$  \hspace{1cm} (2.8)

3) Product yield

The product yield is defined as the amount of desired reagent produced divided by the maximum possible amount of reagent that could be yielded by the input fuel.

The yield of hydrogen and CO is evaluated using Equation 2.9.

$$(H_2+CO) \text{ yield} = \frac{\text{Total mol amount of } H_2 \text{ and } CO \text{ produced per mol of fuel}}{\text{Maximum possible hydrogen and CO production at specific condition}}$$  \hspace{1cm} (2.9)

For example, if C$_{15}$H$_{32}$ is the input fuel and the output contains H$_2$, CO, CH$_4$, CO$_2$, and C$_2$H$_4$, the denominator is the sum of the molar numbers of H$_2$, CO, CO$_2$, 3 times the molar number of CH$_4$, and four times the molar number of C$_2$H$_4$. The liquid is taken as C$_{15}$H$_{32}$, which should give a conservative evaluation for the yield.
4) Fuel conversion

The fuel efficiency is evaluated using the relation prescribed by Equation 2.10:

\[
\text{Fuel Conversion} = \frac{\text{Converted fuel}}{\text{Fuel input}}
\]  

(2.10)

The fuel input is the product of the time and the flow rate. The amount of converted fuel is evaluated using Equation 2.11:

\[
\text{Converted fuel} = \text{Fuel input} - \text{condensed liquid phase products}
\]  

(2.11)

2.1.4 POXR processes

More and more scientists are interested in the catalytic POXR, because the high yields in H\textsubscript{2} and CO can be achieved by operating at very short contact times (\(10^{-2}\text{–}10^{-4}\) s) without steam and/or CO\textsubscript{2}. Non-catalytic POXR processes for gasoline require temperatures in excess of 1,000 °C. These temperatures require the use of special insulation materials and significant preheating and integration of process streams. The use of a catalyst can substantially reduce the operating temperature, allowing the use of more common construction materials such as steel [57] in the reformer. Lower temperature conversion also increases system efficiency. For some heavy hydrocarbon fuels, typical fuel conversion values range from as low as 870 °C for catalytic POX to upwards of 1,400 °C for non-catalytic POX. Using these catalysts
can result in heavy energy penalties as a result of such high temperatures. Lowering the conversion temperature will make this technology much more useful. Table 2.1 shows some commonly used hydrocarbon reforming catalysts.

Table 2.1. Experimental reforming data for temperature range 450-900 °C.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Fuel</th>
<th>Catalyst</th>
<th>Fuel conversion</th>
<th>Hydrogen Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>Heptanes</td>
<td>Rh/γ-Al₂O₃</td>
<td>70%</td>
<td>36%</td>
<td>54</td>
</tr>
<tr>
<td>450</td>
<td>Isooctane</td>
<td>Rh/Al₂O₃</td>
<td>&lt;10%</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>550</td>
<td>Isooctane</td>
<td>Ni-Sn/Ce₀.₇₅Zr₀.₂₅O₂</td>
<td>68%</td>
<td>46%</td>
<td>59</td>
</tr>
<tr>
<td>550</td>
<td>Dodecane</td>
<td>2 % Ni-(Ce₀.₇₅Zr₀.₂₅O₂)</td>
<td>64%</td>
<td>25%</td>
<td>60, 61</td>
</tr>
<tr>
<td>550</td>
<td>Isooctane</td>
<td>Rh/Al₂O₃</td>
<td>30%</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>600</td>
<td>Isooctane</td>
<td>5 wt% Ni/β̃-Al₂O₃</td>
<td>20%</td>
<td>0</td>
<td>62</td>
</tr>
<tr>
<td>600</td>
<td>Isooctane</td>
<td>5 wt% Ni/Ce₀.₇₅Zr₀.₂₅O₂</td>
<td>72%</td>
<td>50%</td>
<td>62</td>
</tr>
<tr>
<td>650</td>
<td>Isooctane</td>
<td>5 wt% Ni/Ce₀.₇₅Zr₀.₂₅O₂</td>
<td>80%</td>
<td>49%</td>
<td>62</td>
</tr>
<tr>
<td>700</td>
<td>Isooctane</td>
<td>Ni-Sn/Ce₀.₇₅Zr₀.₂₅O₂</td>
<td>78%</td>
<td>48%</td>
<td>59</td>
</tr>
<tr>
<td>850</td>
<td>Tetradecane</td>
<td>Rh/Ce₀.₅₆Zr₀.₄₄O₂₋ₓ</td>
<td>&gt;99</td>
<td>81</td>
<td>8</td>
</tr>
<tr>
<td>850</td>
<td>Tetradecane</td>
<td>Pt/Ce₀.₅₆Zr₀.₄₄O₂₋ₓ</td>
<td>97</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>850</td>
<td>Tetradecane</td>
<td>Pt/Al₂O₃</td>
<td>&gt;99</td>
<td>81</td>
<td>8</td>
</tr>
<tr>
<td>900</td>
<td>Tetradecane</td>
<td>0.5 wt% Ru/γ-Al₂O₃</td>
<td>65</td>
<td></td>
<td>63</td>
</tr>
<tr>
<td>900</td>
<td>Tetradecane</td>
<td>La₁.₅Sr₀.₅Ru₀.₀₂Zr₁.₉₅O₇₋₉₋ᵧ</td>
<td>85</td>
<td></td>
<td>63</td>
</tr>
</tbody>
</table>

Table 2.1 shows currently used catalysts for partial oxidation reforming. These catalysts have a good performance at temperatures above 850 °C. Below 850 the performance of the catalysts is poor, even for the precious metal catalysts. Therefore, it is very desirable in the sense of commercial applications to develop a non-precious
catalyst, and increase the reforming performance at low temperatures. A reformer that operates at lower temperatures may result in shorter start-up time and higher efficiency.

2.2 Catalysis and classical promotion

2.2.1 Catalysis

A catalyst is a chemical substance by which the rate of the reaction is increased or decreased. Catalysts may participate in multiple chemical processes but are not consumed by the reaction itself.

![Figure 2.3. Principle energy diagram of catalysis [64].](image)

Positive catalysts work by providing a different transition state with lower activation energy (Figure 2.3). The overall thermodynamics and the final results are
not changed by catalysts. Reagents have to be adsorbed on the surface of solid catalysts before the catalysis process takes place. The diffusion and adsorption of reactants onto the surface is necessary for the chemical reactions on the surface which are followed by desorption and diffusion of products from the surface. The process of a reaction with catalyst can be illustrated in Figure 2.4.

![Diagram of catalysis process](image)

Figure 2.4. Schematic steps of a catalysis process on surface [65, 66].

### 2.2.2 Classical promtion

The term promotion or classical promotion is used to denote the action of a substance, called a promoter, which when added to a catalyst, usually on its surface, enhances the catalytic performance, usually by increasing the rate of catalytic reaction, the selectivity to a desired product, or the useful lifetime of the catalyst [67]. The promoter plays a key role in heterogeneous catalysis, in which the catalyst
exists in a different phase from that of the reactants, [5] and still performs at least one of the above functions.

2.2.3 Classification of the promoter

Promoters are often divided into two kinds: electronic and structural [68-72]. Electronic promoters affect the chemisorptive and catalytic properties of the active phase itself [73]. Or in other words, electronic promoters enhance the catalytic properties of the catalytic phase by affecting the chemisorptive bond strength of adsorbed reactants and intermediates [74]. For structural promoters, the promoting atoms don’t participate themselves in the elementary steps of a catalytic reaction [75]. Instead, they enhance and stabilize the dispersion of the active phase on the catalyst support [74].

2.2.3.1 Electronic promotion, work function and Fermi level

This stems from promoter’s ability to modify the chemisorptive properties of the catalyst surface and to significantly affect the chemisorptive bond strength of reactants and intermediates. At the molecular level this is the result of direct (“through the vacuum”) and indirect (“through the metal”) interactions. The term “through the vacuum” denotes direct electrostatic, Stark type, attractive or repulsive interactions
between the adsorbed reactants and the local electric field created by the coadsorbed promoter, and in the case of attraction may lead to surface compound formation. A “through the metal” interaction refers to a change in the binding state of adsorbed reactants due to promoter-induced redistribution of electrons near the Fermi level of the metal [76, 77]. Energetically, the electron is initially at the Fermi level, \( E_F \), of the solid and energy required to extract an electron from the bulk (\( E_F \)) of the solid through that surface and at a distance of a few \( \mu \)m from the surface [78-80] is called the work function, \( \Phi \). An electropositive promoter decreases the work function of the surface due to the attraction between the positive charge of the electron acceptor and the outer electron of the atom. This in turn weakens the chemisorptive bond of electropositive (electron donor) adsorbates and strengthens the chemisorptive bond of electronegative (electron acceptor) adsorbates. Thus, the catalyst work function \( \Phi \) is shifted in the negative direction when the promoter is electropositive and in the positive direction when the promoter is electronegative.

The work function of a metal is closely related to its Fermi energy, yet the two quantities are not the same. This is due to the surface effect of a real-world solid: a real-world solid is not infinitely extended with electrons and ions repeatedly filling
every primitive cell over all Bravais lattice sites. Nor can one simply take a set of Bravais lattice sites, \{R\}, inside the geometrical region \(V\) which the solid occupies and then fill undistorted charge distribution basis into all primitive cells of \{R\}. Indeed, the charge distribution in those cells near the surface are distorted significantly from that in a cell of an ideal infinite solid, resulting in an effective surface dipole distribution, or, sometimes both a surface dipole distribution and a surface charge distribution.

![Figure 2.5](image_url)

**Figure 2.5.** Relating work function, electron chemical & electrochemical potential.

In Figure 2.5, a schematic representation of the definition of work function \(\Phi\), electrochemical potential of electrons or Fermi level \(\bar{\mu} = E_F\), surface potential is
represented by $\chi$, electrical potential, $\varphi^* (= \varphi$ in the metal and $= \psi$ outside the double layer (dl) $\varphi_\infty^* = \psi_\infty = 0$, where Galvani (or inner) potential is $\varphi$ and Volta (or outer) potential is $\psi$, Fermi energy is $\mu_0$, and the bottom of the conduction band is $E_C$ [62, 81].

As shown in Figure 2.5, the value of the work function is close to the potential drop of the double layer, thus, although the potential drop of the double layer, $\chi$ can’t be measured, it can be well estimated by the work function. Due to the equipotential of the metal, a more positive potential of the metal catalyst can induce a stronger double layer and change the work function significantly, and consequently induce a higher catalytic performance.

When the surface carries a net charge, $q$, then the outer or Volta potential, $\psi$, and the three energies $E_F$, $\Phi$, and $e\psi$ have the following relation:

$$-E_F = \Phi + e\psi$$  \hspace{1cm} (2.12)

When $E_F$ is negative, this means electrons are bound in the solid. $\Phi$ is the energy to bring an electron from the metal Fermi level to a distance, $\delta$, of a few micrometers outside the metal surface, and the energy $e\psi$ is known to surface physicists as the “vacuum level.” It is the energy required to bring the electron from
that position to infinity [82, 83]. Note that these definitions of Φ and ψ are operational, as they introduce the distance δ to overcome the problem of image force interactions [77, 84, and 85]. Thus, the potential φ* shown in Figure 2.5 is the electrical potential according to the jellium model [77, 84, and 85] and ignores image forces. It equals the Galvani potential, φ, inside the metal and the Volta potential, ψ, outside the metal (beyond δ).

\[ E_f \] measures the bulk properties of a metal. The quantities Φ and Ψ are the surface properties which can vary on a metal surface from one crystallographic plane to the next [86, 87]. The work function of the gas exposed surface of the anode can be changed by the gaseous composition [86-92].

When atoms or molecules adsorb on a metal surface they change its work function. Electronegative (electron acceptor) adsorbates such as O or Cl can increase the Φ of the metal surface. Electropositive (electron donor) adsorbates such as H can decrease the Φ of a metal surface [93].
The variation in $\Phi$ of a metal $M$ with the coverage, $\theta_j$, of an adsorbate is given by the Helmholz equation:

$$\Delta \Phi = \frac{eN_M}{\varepsilon_0} \Delta (P_j \theta_j)$$

(2.13)

In Equation 2.13, $e$ is the electron charge ($1.6 \times 10^{-19} \text{C}$), $N_M$ is the surface atom density in atom/m$^2$, $\varepsilon_0$ is the electric permeability of vacuum ($\varepsilon_0$ is the constant $8.85 \times 10^{-12} \text{C}^2/\text{Jm}$), $P_j$ is the dipole moment of the adsorbate, and $\theta_j$ is the coverage in the adsorbed state.

For a discussion of the Volta potential, $\psi$, we make use of Gauss’s law $\oint E \cdot d\Sigma = q_s / \varepsilon_0$, where the integral is over a closed surface $S$, $q_s$ is the charge enclosed by this surface, and $\varepsilon_0$ is the permittivity of the vacuum. When the charge is free to move, the electric field at the metal surface is perpendicular to the surface and is finite on the gas side. Then the Gauss law leads to Equation 2.14,

$$E = \sigma / \varepsilon_0$$

(2.14)

In Equation 2.14, $E$ is the magnitude of the electric field just at the metal surface on the gas side and $\sigma$ is the charge density. For an infinite metal plane, $E$ is then zero everywhere outside the metal. For a finite metal, if $\sigma = 0$, all around the surface, then $E$ vanishes anywhere near the surface, and also at any other point in
space outside the metal; it is uniform and equal to that at infinity, \( \psi_\infty \), which is zero by definition.

2.2.3.2 Structural promoter [94]

There are five kinds of structural promotion: ensemble-size regulating, valence-state promoting, polarizing-structural promoting, surface-phase and cluster complex promotion, and particle stabilizing.

Any catalyst usually has several different surface planes exposed to particles of different sizes. This increases the number of possible reaction paths. Thus, metal catalysts can be considered intrinsically non-selective. The role of promoters or modifiers is to enhance selectivity by changing the active catalyst surface such that the number of reaction paths offered to adsorbed molecules decreases and a selected reaction path dominates. A modifier alters selectivity and activity by introducing the coadsorbate during the reaction from gas to liquid phase. The conditions have to be chosen such that the reaction is thermodynamically feasible.
2.3 Metal-support interaction promotion [95-101]

2.3.1 Metal-support interactions

Conventionally, the catalyst system includes two parts: metal catalyst and catalyst support. Commonly, the catalyst support such as alumina provide a catalyst carrier that prevents sintering or ripening of the active phases to ensure a stable, high active surface area as shown in the following Figure 2.6. However, since 1964, Sinfelt and his coworkers proved the possibility that the effect between metal catalyst and support can alter the catalytic properties of metal catalysts.

Ceria, CeO$_2$, is often used as the support instead of the Al$_2$O$_3$. The experimental results indicated that the performance of the catalyst supported on CeO$_2$ is highly improved. The reason is that using the CeO$_2$ as the catalyst support, the catalyst

![Figure 2.6. Schematic of metal-support interactions.](image-url)
surface is divided in two distinct parts: Part A which is in contact with the support and Part B, which is not in contact with the support. Although CeO$_2$ is a poor oxygen ion conductor; it can still provide the surface oxygen ions for electrocatalytic reactions at Part A. Thus, reforming reaction is promoted at the so-called three phase boundary (TPB). Although a few oxygen ions can backspillover to the metal surface, because the life time of these oxygen ions is very short, they can’t act as the sacrifice promoter for the catalyst system for an extended time. Thus, the reforming reaction can’t be promoted at most of the exposed surface of the metal catalyst but only promoted at the three phase boundary. The size of the area with experiencing promotion is only a few nanometers.

In addition, metal–support interactions with oxygen ion conducting or mixed ionic–electronic conducting supports can enhance the rate of a catalytic reaction only when the reaction is electrophobic.

2.3.2 Spillover-backspillover phenomena

The effect of spillover plays an important role in heterogeneous catalysis and was extensively studied during recent years. It was first noticed in the 1950s by Kuriacose [102], and has been reviewed by Teichner [103] and Conner et al. [104].
The spillover effect can be described as the motion of sorbed species from one phase on which they easily adsorb (donor) to another phase where they do not directly adsorb (acceptor). In this way a seemingly inert material can acquire catalytic activity. In some cases, the acceptor can remain active even after separation from the donor. Also quite often, as shown by Delmon and co-workers [9-11], simple mechanical mixing of the donor and acceptor phases is sufficient for spillover to occur and influence catalytic kinetics leading to a “remote control mechanism,” a term first introduced by Delmon [9]. Spillover may lead not only to an improvement of catalytic activity and selectivity, but also to an increase in lifetime and regenerability of catalysts. If the lifetime of the species by the backspillover is too short, they are consumed soon, desorb to the gas phase, or react with the coadsorbed species.

2.4 Electrochemical promotion; NEMCA; in situ controlled promotion

2.4.1 Phenomena of the NEMCA

Controlled promotion of catalyst surfaces has been a long-sought goal in heterogeneous catalysis, particularly since the 1950s when the importance of the so-called electronic factor was widely recognized [102]. The existence of solid
electrolytes, specific anionic or cationic conductors with negligible electronic conductivity, makes it possible to use electrochemical techniques to study the nature of the promotion effect in catalysts. Application of galvanic cells with solid electrolytes for the study of catalytic phenomena was suggested by Wagner [103]. Later, Vayenas et al. [9-13, and 104] found that upon varying the potential of the working electrode/catalyst, the electrocatalytic (net charge-transfer) reaction rate is affected, as anticipated from Faraday’s Law, but also that the catalytic (no net-charge transfer) reaction rate is changed in a very pronounced, controlled and reversible manner. The increase in the catalytic rate can be up to a factor of 100 times higher than the open-circuit catalytic rate, and up to $3 \times 10^5$ times greater is the change in the electrocatalytic rate. The pronounced reversible promotional phenomena observed upon varying the electrical potential of metal catalysts interfaced with solid electrolytes are known as non-Faradaic electrochemical modification of catalytic activity (NEMCA) [105-108], electrochemical promotion (EP) [109], or in situ controlled promotion (ICP) [110]. As shown in Figure 2.8 the solid electrolyte is yttria stabilized zirconia (YSZ). The promoter is a set of $O^{2-}$ ions that exist in the surface electric double layer of the catalysts.
2.4.2 General feature of the NEMCA

Heterogeneous catalysis and electrochemistry have been traditionally thought to be parts of different scientific domains. The present availability, however, of numerous types of solid electrolytes allows for electrochemical reactions to be carried out at temperatures of catalytic interest. It has thus become possible to use electrochemistry both to study and to influence catalytic phenomena on catalyst surfaces. This interfacing of catalysis and electrochemistry has led to the recent discovery of the effect of NEMCA. The effect underlines some of the fundamental similarities between the two fields [88, 105, 106, 107, 111, and 112-120].

The effect of NEMCA is a catalytic effect taking place over the entire gas-exposed electrode surface and resulting from the electrochemically controlled introduction of dopants from the solid electrolyte onto the gas exposed electrode surface. The kinetics of the introduction of these dopants (O$_2^-$, Na$^+$) onto the catalyst surface is determined by the charge-transfer (electrocatalytic) kinetics at the TPB: catalyst-solid and electrolyte-gas. The term electrocatalytic reaction denotes a reaction where there is a net charge transfer, such as the usual reaction taking place at the metal-stabilized zirconia-gas TPB.
In Equation 2.15, M denotes a surface metal atom while \( O^{\delta^-} - M^{\delta^+} \) denotes the backspillover oxidic species:

\[
O^{2-} (YSZ) + M \rightarrow O^{\delta^-} - M^{\delta^+} + 2 e^-
\]

(2.15)

The backspillover oxide ions \( O^{\delta^-} \) are accompanied by their compensating charge \( \delta^+ \) in the metal, thus forming backspillover dipoles and establishing an effective electrochemical double layer on the gas-exposed catalytically active electrode surface (Figures 2.7 and 2.8).

Figure 2.7. Schematic of reforming of \( C_2H_6 \) with electrochemical promotion.

The backspillover oxygen species primarily occupy the strongly bonded oxygen chemisorptive state. Oxygen adsorbing from the gas phase is forced to
populate primarily the weakly bonded (and highly reactive) state. Therefore, the
backspillover oxide ions are less reactive than normally chemisorbed atomic
oxygen and have a significantly longer lifetime on the catalyst surface.

Thus, the backspillover ions can act as promoters for catalytic reactions taking
place on the gas-exposed electrode surface.

![Effective double layer and classical double layer](image)

Figure 2.8. Effective double layer and classical double layer.

The double layer can’t exactly be measured; however, the potential of the double
layer is similar to the work function shown in Figure 2.5. Thus the effect of the double
layer can be evaluated by measuring the work function. Traditionally, there are two
ways to measure the work function. First way is direct measurement (Kelven Probe).
The second way is indirect measurement (measure the change of the work function)
via measuring the potential of the metal catalyst versus a reference electrode.
The electrochemically (potentiostatically or galvanostatically) induced migration of backspillover dipoles on the catalyst surface is accompanied by a concomitant change $\Delta(e\Phi)$, in the work function, $e\Phi$, of the gas-exposed electrode surface. It is best expressed in the form of Equation 2.16.

$$\Delta(e\Phi) = e \Delta V_{WR}$$  \hspace{1cm} (2.16)

In Equation 2.16, $\Delta V_{WR}$ is the change in the (ohmic-drop-free) catalyst-electrode potential, actually equal to the external applied power. Equation 2.16 is valid even when no migration (backspillover) of ions can take place (e.g. negative current application on metal/YSZ interfaces which also frequently causes NEMCA). In this case, the coverage and dipole moments (therefore also the chemisorptive binding strengths) of covalently bonded adsorbates change to satisfy Equation 2.16.

Positive current application increase $V_{WR}$ and $e\Phi$, resulting in an increasing of the coverage of negatively charged backspillover ions on the gas-exposed catalyst surface. This weakens the chemisorptive bond of electron-acceptor adsorbates (e.g. normally chemisorbed atomic oxygen) and strengthens the chemisorptive bond of electron-donor adsorbates (e.g. olefins or dissociatively chemisorbed hydrogen).
The change in chemisorptive bond strengths with changing catalyst potential and work function is the cause of NEMCA, or EP in catalysis, and leads to the observed dramatic non-Faradaic variation in catalytic rates with $\Delta(e\Phi)$. Linear variation of heats of adsorption, activation energies and logarithms of preexponential factors with $\Delta(e\Phi)$ catalytic rates, $r$, are often found to depend exponentially on $e\Phi$ over wide (0.3 to 1 eV) $e\Phi$ ranges. See the next two equations for a confirmation:

$$\ln\left(\frac{r}{r_0}\right) = \frac{\alpha\Delta(e\Phi)}{k_b T}$$  \hspace{1cm} (2.17)  \\
$$\ln\left(\frac{r}{r_0}\right) = \frac{\alpha V_{WR}}{RT}$$  \hspace{1cm} (2.18)

In Equations 2.17 and 2.18, $\alpha$ is positive for electrophobic reactions and negative for electrophilic ones. The sign and magnitude of $\alpha$ (typically -1 to +1) depends primarily on the polarity of the (partially ionic) chemisorptive bonds broken and formed in the rate limiting step of the catalytic reaction.

### 2.4.3 Key aspects of electrochemical promotion

According to Vayenas et al., [6-8] the NEMCA effect can be described by the following parameters.
The rate enhancement ratio was defined in Chapter 1, as shown in the following equation:

\[ \rho = \frac{r}{r_0} \]  \hspace{1cm} (1.1)

Due to the strong lateral repulsive interactions between the parallel-oriented surface dipoles, the migration of these dipoles on the catalyst surface is fast. The rate of migration is not limited by the surface diffusion but rather by the rate, \( I/nF \), of creation of the surface dipoles at the TPB of metal-solid electrolyte-gas. Consequently, the time \( \tau \), required to form the “effective electrochemical double layer” during galvanostatic transients is of the order of Equation 2.19:

\[ \tau = \frac{nFN\theta_i}{I} \]  \hspace{1cm} (2.19)

In Equation 2.19, \( n \) is the absolute value of the ion charge, \( N \) is the number of moles of the gas-exposed catalyst surface, \( \theta_i \) is the established steady-state surface coverage of the migrating ions (dipoles) and \( I \) is the applied current.

The enhancement factor or Faradaic efficiency, \( \lambda \), was defined from Equation 1.2:

\[ \lambda = \frac{\Delta r_{\text{catalytic}}}{(I/2F)} \]  \hspace{1cm} (1.2)

This is positive for electrophobic reactions and negative for electrophilic ones.

The Faradic efficiency is a key parameter. The order of magnitude of the absolute
value, $|\lambda|$, of the Faradaic efficiency $\lambda$ can be estimated for any reaction from the following Equation 2.20:

$$|\lambda| = \frac{2F r_\theta}{I_0}$$  \hspace{1cm} (2.20)

In the previous formula, $r_\theta$ is the open-circuit catalytic rate (expressed in mol O) and $I_0$ is the exchange current of the metal-solid electrolyte interface during the catalytic reaction, extracted from the usual Tafel plots. The derivation of equation (2.20), which is in good agreement with measured $\lambda$ values of some 30 catalytic reactions (ranging from 1 to $10^5$) is simple and has been presented elsewhere. It stems from the exponential dependence of the rates of catalytic, $r$, and electrocatalytic, $I/2F$, reactions on catalyst-electrode potential. The predictions of Equation 2.20 are almost quantitative when the absolute value $|\alpha|$, of the NEMCA coefficient, $\alpha$, is close to the values of the anodic ($I > 0$) or cathodic ($I < 0$) transfer coefficients $\alpha_a$ and $\alpha_c$.

The parameter $I_0$ is usually proportional to the TPB length and can be largely controlled by appropriate choice of the sintering temperature during catalyst film preparation.

Equation 2.20 is quite important, as it defines the limits of applicability of NEMCA ($|\lambda|>>1$). In order to observe a non-Faradaic rate enhancement (NEMCA),
the open circuit rate, $r_0$, of the catalytic reaction must be larger than the
electrocatalytic exchange rate $I_0/2F$. In simple terms the catalytic reaction must be
faster than the electrocatalytic one.

2.4.4 Summary

The effective electrochemical double layer established on the gas-exposed
catalyst-electrode surface affects the binding strength of covalently bonded adsorbates,
chemisorbed reactants and reaction intermediates. These may or may not occupy the
same type of surface sites as the backspillover ions.

The binding strength of adsorbates is affected due to both direct electrostatic
interactions in the effective double layer (i.e. through the vacuum interactions), and
through the metal interactions.

The NEMCA effect does not appear to be limited to any specific type of catalytic
reaction, metal catalyst or electrolyte, particularly in view of the recent demonstration
of NEMCA using aqueous electrolytes. The catalyst, however, must be electronically
conductive and the only report of NEMCA on an oxide catalyst is for the case of IrO$_2$
which is a metallic oxide. It remains to be seen if NEMCA can be induced on
semiconductor catalysts.
2.5 Interrelationship between catalysis, classical promotion, metal-support interaction and electrochemical promotion

2.5.1 Catalysis, classical and electrochemical promotion example [13]

In order to compare the catalysis of chemical and electrochemical promotion, a classical example is given. The reaction under consideration is the reduction of NO by CO in presence of O_2. This is a complex reaction system but was of great technological importance for the development of efficient catalytic converters to be able to treat automobile exhaust gases.

![Graph showing CO_2 and N_2 formations under open-circuit conditions](image)

(a)

In Figure 2.9, (a) and (b) are the CO_2 and N_2 formations, respectively, under open-circuit (o.c.) conditions, upon application (via a potentiostat) of catalyst
potential values, $U_{WR}$, of +1 and -1 V. Icons mean (○) for catalysis, (□) for classical promotion, and (●,♦) for electrochemical promotion of a classically promoted (sodium doped) substance (■,▲) [2].

Figure 2.9. Temperature dependence of catalytic rates and turnover frequencies.

The desired product is $N_2$, as opposed to $N_2O$ and a good catalyst must not only catalyze NO reduction at as low a temperature as possible (preferably below 200 °C), but must also exhibit good selectivity to $N_2$. 
The main reactions are given in Equations 2.21 - 2.23. The selectivity of a catalyst to diatomic nitrogen, $S_{N_2}$, is defined by Equation 2.24.

$$2\text{CO} + 2\text{NO} \rightarrow \text{N}_2 + 2\text{CO}_2 \quad (2.21)$$

$$\text{CO} + 2\text{NO} \rightarrow \text{N}_2\text{O} + \text{CO}_2 \quad (2.22)$$

$$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \quad (2.23)$$

$$S_{N_2} = \frac{r_{N_2}}{r_{N_2} + r_{N_2\text{O}}} \quad (2.24)$$

2.5.1.1 Electrochemical promotion situation

Electrochemical promotion of the unpromoted Rh/YSZ film, via application of 1 to -1 V, leads to a significant rate enhancement (tenfold increase in $r_{\text{CO}_2}$, fourfold increase in $r_{N_2}$ (●,♦ in Figure 2.9).

2.5.1.2 Classical promotion situation

Then the same Rh film has been classically promoted by depositing on its surface 1 µL of a $10^{-2}$ N NaOH solution, followed by drying and thorough H$_2$O evaporation in a classical “dry impregnation” process. The resulting promoted Rh film exhibits now a dramatic enhancement in its catalytic performance, as shown by the curve labeled “classical promotion” in Figure 2.9 (□). Its “light off” temperature has been decreased by 150 °C and the $N_2$ selectivity, $S_{N_2}$, has been enhanced.
Therefore sodium (or NaβOH) is an excellent promoter of Rh for this reaction, and it came directly from an electrochemical promotion investigation of the same reaction on Rh films deposited on a -βAl₂O₃, a Na⁺ conductor. That study, as with previous ones using Pt films, had shown that sodium, electrochemically supplied, in the form of Na⁺, to the precious metal catalysts Pt, Pd, and Rh, enhances dramatically the catalytic properties of the precious metal catalyst-electrode. The main reason is that Na further enhances NO dissociation.

2.5.1.3 Electrochemical promotion of a promoted catalyst promotion situation

Consider a case when the promoted Rh catalyst is deposited on the YSZ. If an external voltage of \( U_{WR} \) (±1V) is added, and the concomitant supply (+1V) removed (-1V) of \( O^{2-} \) to or from the surface of the promoted Rh surface, the result is shown in Figure 2.9 with the curves labeled “electrochemical promotion of a promoted catalyst”. It is clear that positive potentials, i.e. supply of \( O^{2-} \) to the catalyst surface, further enhances its performance. The light-off temperature is further decreased and the selectivity is further enhanced, because of the effect of the external potential \( U_{WR} \) on the chemisorptive bond strength of various adsorbates, such as CO, NO, N and O. But the fact is that positive potentials (+1V) can further
significantly enhance the performance of an already promoted catalyst. So one can
electrochemically promote and already classically promote a catalyst.

From Figure 2.9, one might find that negative potentials, \( U_{WR} = -1 \text{V} \) fail to
further enhance to any significant extent catalyst performance of the promoted
catalyst, but the unpromoted Rh catalyst is electrochemically promoted with both
positive and negative potentials. This is because negative potential application is
equivalent to alkali supply on the catalyst surface. They both lead to a substantial
decrease (up to 2-3\text{eV}) in the catalyst work function, \( \Phi \), a quantity which plays an
important role in the description of promotion and electrochemical promotion.
Consequently a metal catalyst, already promoted with an alkali, and thus having
already a low work function, \( \Phi \), can only be marginally affected by negative
potential application.

2.5.1.4 Catalysis promotion situation

Without a catalyst there is no \( \text{N}_2 \) and \( \text{CO}_2 \) production below 600 °C [121].
When using a polycrystalline Rh film of mass \( m_{\text{Rh}} = 2 \text{ mg} \), and specific surface area
of \( N_{\text{Rh}} = 10^{-7} \text{ mol} \), one obtains the curve labeled “catalysis” in Figure 2.9. It is worth
pointing out that Rh is the best known precious metal catalyst for NO reduction due
to its ability to chemisorb NO dissociatively, to a large extent. This Rh film is deposited on YSZ (Y$_2$O$_3$-stabilized –ZrO$_2$), an O$^{2-}$ conductor, but the rate versus T curves in Figure 2.9 labeled “catalysis” (○) have been obtained under open-circuit (o.c.) conditions, i.e. without any current or potential application. They thus reflect, to a large extent, the inherent catalytic properties of Rh for NO reduction, without the aid of chemical promotion.

### 2.5.2 Summary of the conventional ways for catalyst promotion

1) Catalysts

   By the very nature of catalysts, they serve to increase reaction rates. Catalysts can also decrease the temperature at which reactions can begin, or in other words, lower the activation energy of the reaction.

2) Catalysts with support

   Traditionally, the catalyst is made from metal catalyst and catalyst support, because the catalyst support can provide a carrier for the metal catalyst and prevent the coking problem [189-196] of metal catalysts.
Metal catalyst deposited on a support can get a higher specific surface area and more active sites for the reactions to take place.

3) Classical promoters

The review of the classical promotion reveals that the performance of the catalyst system can be improved by depositing promoters (NaCl, NaOH) [95, 96] on
the surface of metal catalyst. These promoters change the work function of the metal
catalyst and modify the chemisorptive properties of the catalyst surface, which
significantly affect the chemisorptive bond strength of reactants and intermediates.

Finally, the specific surface area of the catalyst is promoted.

4)  Metal-support interaction - TPB promotion

As mentioned in the review, the solid electrolyte can provide the surface
oxygen ions necessary for the reforming reactions at the TPB.

The net-charge transfer (electrocatalytic reaction) at the TPB is promoted. In
addition, the lifetime of the surface oxygen ions is very short. Thus, using solid
electrolyte as the catalyst support, the activity of the catalysts at TPB area is
promoted.
The difference between metal-support interactions and electrochemical promotion is that the active site of electrocatalysis is not limited to the TPB for electrochemical promotion. Due to a continual supply of oxygen ions and the action of ion spillover, this active zone can extend over the entire gas-exposed electrode surface. These spillover species are accompanied by their image charge in the electrode and thus, in addition to the classical double layer present at the electrode/electrolyte interface, a second double layer is formed at the electrode/gas interface (Figure 2.8) which is commonly termed the “effective” double layer.

5) Electrochemical promotion - TPB and specific surface area promotion

Electrochemical promotion is functionally identical to classical promotion; i.e., it is catalysis in the presence of a controllable double layer at the metal/gas interface.
The main advantage of electrochemical promotion is that it also allows the use of short-lived sacrificial promoters [129-134], which are promoters forcing oxygen to populate the weakly bonded and highly reactive oxygen adsorption state, such as O$_{2}^-$, which are continuously supplied to the catalyst/gas interface via electrochemical promotion.

Figure 2.13. Schematic of the electrochemical promotion.
2.5.3 Novel self-sustained electrochemical promotion catalysts system

The performance of the catalyst can be significantly improved by electrochemical promotion. However, this kind of catalyst system is not easy to be realized, because it needs an external power source.

The new concept self-sustained electrochemical promotion catalysts, as illustrated in Figure 2.14, without external power, can take advantage of normal electrochemical promotion, and be easily prepared. It can enable a coupling of different functional components in microscopic (nm) and macroscopic domains (~mm), thereby greatly increasing the reaction kinetics.

![Figure 2.14. Schematic of self-sustained electrochemical promotion catalysts.](image)
2.6 Instrument analysis

Gas chromatography, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffractometry (XRD), transmission electron microscopy (TEM) and specific surface area ASAP 2010 machines have been applied to analyze the production and characterize the catalysts and catalyst supports.

2.6.1 Gas chromatograph

A gas chromatograph, or GC, is a chemical analysis instrument for separating chemicals in a complex gaseous sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically [137].

The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time). Other parameters that can be used to alter the order or time of retention are the
carrier gas, flow rate, and the temperature. In a GC analysis, a known volume of
gaseous or liquid analyte is injected into the "entrance" (head) of the column,
usually using a microsyringe (or solid phase microextraction fibers, or a gas source
switching system).

As the carrier gas sweeps the analyte molecules through the column, this
motion is inhibited by the adsorption of the analyte molecules either onto the
column walls or onto packing materials in the column. The rate at which the
molecules progress along the column depends on the strength of adsorption, which
in turn depends on the type of molecule and on the stationary phase materials. Since
each type of molecule has a different rate of progression, the various components of
the analyte mixture are separated as they progress along the column and reach the
end of the column at different times (retention time) [138]. A detector is used to
monitor the outlet stream from the column; thus, the time at which each component
reaches the outlet and the amount of that component can be determined. Generally,
substances are identified qualitatively by the order in which they emerge (elute)
from the column and by the retention time of the analysis in the column.
2.6.2 SEM

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, and composition. Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. The specimens for SEM tests must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Nonconductive or resistive specimens tend to charge when scanned by the electron beam, therefore they usually are coated with an ultrathin coating of electronically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Coating prevents the accumulation of static electric charge on the specimen during electron irradiation and increases signal and surface resolution, especially with samples of low atomic number (Z).
2.6.3 EDAX

Since each element has a unique atomic structure, Energy dispersive X-ray spectroscopy (EDAX or EDS) could be used for the elemental analysis through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. EDAX systems are most commonly found on scanning electron microscopes (SEM-EDAX) and electron microprobes. A detector is used to convert X-ray energy into voltage signals and sends them to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis. As shown in Staiti’s paper [139], EDAX analyses were performed on different regions of each sample to determine representative values of potassium contents. Thus an atomic ratio calculated from EDAX is considered representative for all the samples.
2.6.4 XRD

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction. X-ray crystallography is a method of determining the atom arrangement within a crystal or the crystalline structure of materials such as the size of atoms, the lengths and types of chemical bonds, and the atomic-scale differences. XRD can be used to measure the average distance between layers or rows of atoms, determine the orientation of a single crystal or grain, find the crystal structure of an unknown material, and measure the size, shape and internal stresses of small crystalline regions [140].

For many catalysts, at least, the effect of the promoters on the physical structure is of primary importance. This type of effect is directly amenable to study by X-ray diffraction methods. These methods can give information regarding the atomic position in solids, the probable limits of crystal size, and the existence of solid solutions. They can, however, yield no knowledge of the conditions existing at the surface where catalytic action undoubtedly takes place [141].
A crystal lattice is a three dimensional arrangement of atoms. These atoms are arranged in a series of parallel planes separated by a distance, d. For a crystal, planes exist in a number of directions-each with its own interplanar spacing d.

![Figure 2.15. Bragg diffraction.](image)

The two parallel incident rays have an angle with these planes (θ). The most intense reflection beam occur when the two waves are in phase. That is, reflection beam with maximum intensity occurs when the difference of path length between A-B and A’-B’ is an integral number of wave length, such that

\[ 2d \sin \theta = n \lambda \]  

(2.25)

2.6.5 TEM

TEM is an indispensable tool in visualizing mesoporous materials. The bright-field images collected using a TEM, similar to those of the light microscope,
reveal the internal components of the sample. Because electrons generate the sample image, TEM images are only available in black and white. In order to obtain a high-quality image, the sample must also be thin enough for the electron beam to pass through; therefore, sample preparation is a key step in acquiring high-quality TEMs. TEM, operating under high-vacuum conditions, has a greater resolving power and a higher magnification range than the light microscope. The TEMs resolving power is related to the wavelength and numerical aperture of a lens. It typically produces a 1,000-fold increase in resolving power over the light microscope. In contrast to the light microscope, diffraction can be a very useful tool in TEM because it differentiates between “holes” and solid surfaces. Also, unlike SEM, a sizeable portion of the TEM sample is illuminated with the electron beam because it operates in a flood-beam manner. One can then visualize the mesopore structures, confirming XRD measurements.

2.6.6 Specific surface area measurement

Specific surface area measurement, also called BET after the first initials of Burnauer, Emmett, and Teller, refers to the method of measuring the specific surface area and porosity of solid materials using the principals of physical adsorption and
de-sorption of gas [142]. The Micromeritics ASAP 2010 (Accelerated Surface Area
and Porosimetry System) provides high quality specific surface area (BET) and
porosity measurement on different types of solid materials based on the gas
adsorption theory. Carbon nanotubes and catalysts are characterized using this
technique. The Micromeritics ASAP 2010 system consists of an analyzer equipped
with two sample preparation ports and one analysis port, a control module, and an
interface controller which helps the operation to be controlled easily and accurately.
In addition, the Micromeritics ASAP 2010’s software allows us to perform
automatic analysis and collect a variety of analysis reports.

![Diagram](image)

Figure 2.16. How specific surface area of small particles is measured.

The gas adsorption method is a method for measuring the amount of gas
adsorbed on the surface of a powder sample as a function of the pressure of the
adsorbate gas, and is used to determine the specific area of a powder sample (Figure
2.16).
Measurements are usually performed at the boiling point of liquid nitrogen (-196 °C). Specific surface area is generally expressed in units of m$^2$/g. If the gas is physically adsorbed by the powder sample, when $P/P_0$ is in the range of 0.05 to 0.3, the following relationship holds:

$$\frac{1}{V_a(P_0/P - 1)} = \frac{(C - I)}{V_mC} \times \frac{P}{P_0} + \frac{I}{V_mC} \quad (2.26)$$

In Equation 2.26, $P$ is the partial vapor pressure of adsorbate gas in equilibrium (kPa) [143], $P_0$ is the saturated pressure of the adsorbate gas at -196 °C, $V_a$ represents the volume of gas adsorbed at equilibrium (mL), $V_m$ is the volume of gas adsorbed in monolayer (mL), and $C$ is a dimensionless constant related to the enthalpy of adsorption and condensation of the adsorbate gas.
Equation 2.26 is an adsorption isotherm and can be plotted as a straight line with $1/V_a \cdot [(P_0/P) - 1]$ on the y-axis and $\varphi = P/P_0$ on the x-axis according to experimental results. This plot is called a BET plot.

![BET plot](image)

Figure 2.17. BET plot for specific surface area calculation.

The linear relationship of this equation is maintained only in the range of $0.05 < P/P_0 < 0.35$. The value of the slope $A$ and the y-intercept $I$ of the line are used to calculate the monolayer adsorbed gas quantity $V_m$ and the BET constant $C$. The BET method is widely used in surface science for the calculation of specific surface area of solid by physical adsorption of gas molecules [144].
The following set of equations can be used to calculate the slope and y-intercept of any BET plot like the one shown in Figure 2.17.

\[ V_m = \frac{I}{A + I} \]  \hspace{1cm} (2.27)

\[ C = I + \frac{A}{I} \]  \hspace{1cm} (2.28)

A total surface area \( S_{total} \) and a specific surface area \( S \) are evaluated by the following two equations.

\[ S_{BET, total} = \frac{V_m N_s}{V} \]  \hspace{1cm} (2.29)

In Equation 2.29, \( V_m \) is in units of volume which are also the units of the molar volume of the adsorbent gas. From Equation 2.29, it is easy to arrive at the following equation.

\[ S_{BET} = \frac{S_{total}}{a} \]  \hspace{1cm} (2.30)

In the above equation set, \( N \) is Avogadro’s constant, \( s \) is adsorption cross section of the adsorbing species, \( V \) is the molar volume of adsorbent gas, and \( a \) is the mass of adsorbent in grams.

2.7 Summary

As for the CPOX process, good catalysts can enhance reaction rates, and repudiate high temperature reforming necessities. Therefore, it allows for large-scale
use of more common materials like steel, in the design of the reformer, and results in low cost. However, to this day, most CPOX catalysts are precious metal-based. In addition, their CPOX process temperature is still very high (>700 °C).

As mentioned, the classical promotion catalyst, metal-support interactions catalyst, and the reforming catalyst only can take place at the nano-sized three phase boundary (metal/electrolyte/gas) points. Electrochemical promotion can supply the sacrificial promoters continuously and get a higher promotion for the reaction than the classical promotion. However, it is not easy to be realized.

Based on the review, this thesis presents an approach to prepare new catalysts. The new concept of catalysts can enable electrochemical promotion without an external power source and can enable coupling of different functional components in microscopic (nm) and macroscopic domains (~mm), thereby greatly increasing the reaction kinetics. The activity and resistance to coking of the catalytic active phases are enhanced with a large self-sustained flux of short-lived promoters. The catalysts can enable catalytic reactions with high reaction rates at temperatures much lower than those required for conventional catalysts resulting in an increase of specific energy, specific power, and efficiency, along with a reduction of cost.
A number of analytical tools such as XRD, SEM, EDS and BET specific surface area/pore-size measurements are used to examine the stability, phase purity, morphology, porosity, chemical properties of various components used in constructing the catalysts.
CHAPTER 3 EXPERIMENTAL

This chapter presents the catalyst preparation, including the selection of materials, equipment, and the process. In addition, the catalyst performance evaluation system and the characterization methods are also presented.

3.1 Materials

The trade names, chemical names, molecular weights, concentration/purity, and sources of the materials used in this dissertation are listed in Table 3.1. Strontium-doped LaMnO$_3$ (LSM) or lanthanum strontium cobalt ferrite (LSCF) is selected as the cathode phase. Ceria, Ni and Cu are selected for the anode phase. Ni and Cu also act as the electron conductor. Yttria-stabilized zirconia (YSZ) or Gadolinium doped ceria (GDC) is selected as the oxygen ion conductor. During the catalyst support preparation, the dispersant can mixed the slurry uniformly. The binder can bind the YSZ/GDC with LSM/LSCF uniformly. The PMMA and graphite turn the catalysts into porous structures.
The ingredients of the newly devised SSEP catalysts are presented below, in Table 3.1.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Trade name</th>
<th>Molar Weight</th>
<th>State/Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>Yttria-stabilized zirconia</td>
<td>123.22</td>
<td>Powder, fuelcellmaterials.com</td>
<td></td>
</tr>
<tr>
<td>GDC</td>
<td>Gadolinium doped ceria</td>
<td>513.64</td>
<td>Powder, fuelcellmaterials.com</td>
<td></td>
</tr>
<tr>
<td>LSM</td>
<td>Strontium-doped LaMnO3</td>
<td>236.71</td>
<td>Powder/99.99 wt%, PRAXAIR</td>
<td></td>
</tr>
<tr>
<td>LSCF</td>
<td>Lanthanum strontium cobalt ferrite</td>
<td>222.85</td>
<td>Powder, fuelcellmaterials.com</td>
<td></td>
</tr>
<tr>
<td>Ni(NO₃)₂ · 6H₂O</td>
<td>Nickel(II) nitrate hexahydrate</td>
<td>290.81</td>
<td>Flake/98 wt%, Alfa Aesar</td>
<td></td>
</tr>
<tr>
<td>Cu(NO₃)₂ · 3H₂O</td>
<td>Copper(II) nitrate trihydrate</td>
<td>241.60</td>
<td>Crystalline lumps/98 wt%, Alfa Aesar</td>
<td></td>
</tr>
<tr>
<td>Ce(NO₃)₃ · 6H₂O</td>
<td>Cerium(III) nitrate hexahydrate</td>
<td>434.22</td>
<td>Crystalline aggregates, 99.5 wt%, Alfa Aesar</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>C</td>
<td>12.01</td>
<td>Powder, Cabot corporation</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
<td>1.3 g/mL</td>
<td>Aldrich</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>Distilled water</td>
<td>18.02</td>
<td>Liquid, FIU</td>
<td></td>
</tr>
<tr>
<td>Dispersant</td>
<td>DURAMAX D-3005 polymer</td>
<td>~2400</td>
<td>Pale yellow liquid, Dow</td>
<td></td>
</tr>
<tr>
<td>Binder</td>
<td>DURAMAX B-1022</td>
<td>1.08 g/mL</td>
<td>Dow</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Equipment

Information about equipment used in this dissertation is listed in Table 3.2.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Model</th>
<th>Precision</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precision Weighing Balances</td>
<td>ALC-204</td>
<td>±0.0001 g</td>
<td>Acculab</td>
</tr>
<tr>
<td>Magnetic Stirring Hot Plate</td>
<td>Stable Temp</td>
<td>±1 °C</td>
<td>Cole-Parmer</td>
</tr>
<tr>
<td>Lindberg Furnace</td>
<td>BF51314C</td>
<td>±0.1 °C</td>
<td>Lindberg/Blue</td>
</tr>
<tr>
<td>Gas Chromatograph</td>
<td>6890N</td>
<td>n/a</td>
<td>Agilent</td>
</tr>
<tr>
<td>Pump</td>
<td></td>
<td>0.1 mL/min</td>
<td>LabAlliances</td>
</tr>
<tr>
<td>Benchtop Thermal Controllers</td>
<td>MCS-2110</td>
<td>±1 °C</td>
<td>Omega Engineering Inc.</td>
</tr>
<tr>
<td>Temperature PID controller</td>
<td>96VFL13</td>
<td>±1 °C</td>
<td>EXTECH Instruments</td>
</tr>
<tr>
<td>K type thermocouples</td>
<td>GA30374</td>
<td>±1 °C</td>
<td>McMaster-Carr Supply Co.</td>
</tr>
<tr>
<td>Digital Flow meter</td>
<td>FMA 6500</td>
<td>±0.1 mL/min</td>
<td>Omega</td>
</tr>
<tr>
<td>Digital Pressure Gauges</td>
<td>DPG1100</td>
<td>±0.25 %</td>
<td>Omega Engineering Inc.</td>
</tr>
</tbody>
</table>

3.3 Preparation of the SSEP catalysts

3.3.1 Preparation of SSEP catalysts support

The basic procedure for the preparation of SSEP catalyst supports is shown in Figure 3.1. Yttria-stabilized zirconia (YSZ), \((\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}\) (8 mol% Yttrium, YSZ8-U1, specific surface Area 10.4 m\(^2\)/g), Gadolinium doped ceria (GDC),
Gd$_{0.10}$Ce$_{0.90}$O$_2$ (10 mol% Gadolinium, GDC-10-M, specific surface Area 34.3 m$^2$/g), and La$_{0.9}$Sr$_{0.1}$MnO$_3$ (LSM) with a particle size range of 0.3-0.5 µm were used to prepare catalysts.

![Basic procedure for catalyst synthesis](image)

Figure 3.1. Basic procedure for catalyst synthesis.

Firstly, the oxygen ion conductor (YSZ or GDC), cathodic catalysts LSM, fine graphite powder (Cabot corporation VULCAN XC72R GP-3860), and polymethyl methacrylate (PMMA) powder were mixed into deionized water with additions of dispersant and binder to make a slurry. Secondly, the slurry was casted on a plate and dried at room temperature and then calcinated at 1200 °C for four hours for
YSZ-based catalyst (or 1100 °C for four hours for GDC-based catalyst). Graphite and PMMA would be completely burned during calcination to form very fine (20 nm) and large (0.2 µm) pores respectively.

### 3.3.2 Preparation of the SSEP catalysts

The material was ball-milled to fine powder (≤10 µm) and then impregnated with saturated Ni, Ce and Cu nitrate solution. The solution was dried at about 120 °C for 2 hour and fired at 500 °C for four hours to transform the nitrides into oxides. The resulting powder was reduced by passing hydrogen at 520°C for about four hours. The metal particles spread in the pores of the support, YSZ and LSM or GDC and LSM. The mass ratio of YSZ/GDC to LSM was 1:1. The actual compositions are shown in Table 3.3.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>YSZ, wt%</th>
<th>LSM, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>Ce, wt%</th>
<th>Pt, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ-based</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt/CeO₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>97.6</td>
<td>2.4</td>
</tr>
</tbody>
</table>

As opposed to the catalyst support preparation process shown in Figure 3.1, the overall catalyst production process is illustrated in Figure 3.2.
This process is very much like the catalyst support fabrication process, only it has another step involved, the reduction stage.

Figure 3.2. Basic procedures for catalyst synthesis.

3.4 Catalytic performance evaluation

In this research, the liquid $\text{C}_{15}\text{H}_{32}$ was used to evaluate the catalytic performance of the SSEP catalysts. Partial oxidation reforming tests were conducted using a fixed bed reforming apparatus as schematically shown in Figure 3.3 (a) and (b). The main reactor is a 0.5” stainless steel tube (SS 316). The catalysts was mixed with quartz
beads (Length 2 mm, Diameter 2 mm, Quartz Scientific Inc.) and loaded in the reforming reactor.

![Diagram](image)

(a)

The mass ratio of catalyst to quartz beads is 1:1. The catalyst section is 4 cm long on the lower part of the reactor and contains only 4 g of catalysts. The operation temperature is controlled using thermal controller (MONOGRAM, Omega) with K type thermocouples (GA30374, McMaster-Carr Supply Co.) and a heating tape (STH051-020, Omega). The air stream is regulated with a back pressure regulator and a digital flow meter (FMA 6500 digital mass flow controller, Omega). Liquid
hydrocarbon n-pentadecane (Alfa Aesar, purity 99.9%) is pumped with a simple metering pump at 0.1 mL/min (LabAlliances). Before the air and fuel reach the inlet of the reactor, a funnel-shaped fuel/air mixer is required to achieve a uniform mixing of air and fuel. The output is first condensed in a condenser at about 0 °C and then sent to a gas chromatography (GC, Agilent 6890N) with a TCD detector.

Figure 3.3. Fixed bed reforming apparatus (a) diagram & (b) photograph.

3.5 Characterization

SEM/EDS have been the most commonly used tool to characterize the morphology and topology of different samples. A series of SEM and EDS analyses
were conducted on entire catalysts samples that were evaluated in this research. The SEM/EDS facility used in this study is XL30 ESEM-FEG from Philips. The powder samples were mounted on the standard specimen stubs with the help of double adhesive tape and carbon paste. The samples were coated with a thin layer of Pd using Cressington sputter coater 108 auto to ensure sufficient conductivity. The electron beam parameters were kept constant during the analysis of the entire sample. The micro-graph of the samples with 20 kV EHT and 25 pA beam current were recorded by a 35 mm camera attached on the high resolution recoding unit. In addition, the EDS X-ray spectrometer was used, and was attached to the SEM system to analyze the distribution of elements on the surface. The accelerating voltage for EDS analysis was 20 kV.

X-ray diffraction (XRD, Seifert diffractometer) techniques were used for the examination of morphology and structure of the catalysts obtained in this work. XRD experimentation was conducted on the membranes with an automated X-ray diffraction system configured with a theta/two-theta goniometer, fitted with a Peltier-type solid-state detector at a scan rate of 0.02 °C/min and a step of 0.04 °C. Data was taken before and after heating the film. The XRD beam penetrated the
sample to a depth of 10–15 Å, which ensured that only the bulk polymer on top of the pores was being examined.

The TEM examinations were carried out in a JEOL JEM-1400 electron microscope; the energy of the electron beam was 100 kV. A resolution of 0.5 nm and a magnification of $3 \times 10^5$ was used.

The specific surface area and porosity information was obtained through gas physisorption (BET analysis) using a Micromeritics ASAP 2020.
In this chapter, firstly, the performances of SSEP catalysts are compared with that of precious metal catalyst, including the commercial precious catalyst, 2 wt% Pt/CeO$_2$ and an Rh-based catalyst. Secondly, in order to confirm the existence of the SSEP, catalyst YNCCe without LSM and catalyst LNCCe without YSZ were synthesized and evaluated in the same POX reforming reactor. The experimental results prove the existence of the self-sustained electrochemical promotion.

4.1 POXR results for SSEP catalysts

POX reforming experiments were conducted for the two catalysts with compositions shown in Table 4.1 at different temperatures from 450 to 650 °C. The first catalyst was synthesized according to the procedure shown in Figure 3.2, while the second catalyst was acquired from FuelCellMaterials.com. The description of this Pt/CeO$_2$ catalyst claims that this catalyst is for hydrocarbon reforming at temperatures ranging from 400 to 800 °C. In this research, this sample is used as a reference.

Appropriate flow rates were 0.01 mL/min for the fuels and 200 mL/min for air.

The pressure throughout this experimental work is about 1.34 atm. GC
spectroscopy indicates the major gas phase products are hydrogen, carbon monoxide, methane, and oxygen or nitrogen.

Table 4.1. Components of an SSEP and a commercial promotion catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>YSZ, wt%</th>
<th>LSM, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>CeO₂, wt%</th>
<th>Pt, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YLNCCe</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt/CeO₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>98</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 4.1. Fuel conversions of SSEP catalyst YLNCCe & commercial catalyst Pt/CeO₂.

Figure 4.1 compares the fuel conversion of the SSEP YLNCCe catalyst to a commercially available catalyst, Pt/CeO₂. It is clear that the fuel conversion of SSEP catalysts is much better than that of the commercial Pt/CeO₂ catalyst at lower
temperatures. Fuel conversion is 98% for SSEP YLNCCe catalysts and under 10% for Pt/CeO$_2$ catalyst at 450 °C. However, fuel conversion is 100% for both SSEP YLNCCe catalyst and Pt/CeO$_2$ catalyst at 650 °C.

As shown in Figure 4.2, the yield of H$_2$+CO increases as a function of temperature. The yield of H$_2$+CO is 19.7% for SSEP YLNCCe catalyst while virtually 0% for Pt/CeO$_2$ catalyst at 450 °C. The yield of (H$_2$+CO) is 90% for SSEP YLNCCe catalyst and 81.6% for Pt/CeO$_2$ catalyst at 650 °C.

In order to verify the accuracy of the experimental system and results, the ratio
of O/N and ratio of O\textsubscript{in}/O\textsubscript{out} were examined at the outlet. The input air in the atmosphere contains 20.9% O\textsubscript{2} and 78.08% N\textsubscript{2}. Therefore, the ratio of O/N, \( \eta \), should be 26.8% at the outlet. The ratio of O/N was calculated using the following equation assuming that most of O is combined into CO and CO\textsubscript{2}:

\[
\eta = \frac{\nu\%CO + 2 \times \nu\%CO_2}{2 \times \nu\%N_2}
\] (4.1)

where \( \nu\% \) is the molar percentage. As can be found from Figure 4.3,

![Figure 4.3. Ratio of O/N for the SSEP catalysts and Pt/CeO\textsubscript{2} catalyst.](image)

the average ratio of O/N does vary around 26% and the average is 24.02% with a variance of \( \pm 5\% \).
The ratio of amount of O at inlet to that at outlet, $\omega$, was also calculated using the following equation:

$$\omega = \frac{2 \times \text{v}\%\text{N}_2 \times 0.27}{\text{v}\%\text{CO} + 2 \times \text{v}\%\text{CO}_2}$$  \hspace{1cm} (4.2)$$

As shown in Figure 4.4, the average ratio of $O_{\text{In}}/O_{\text{Out}}$ is 0.95.

![Figure 4.4. Oxygen inlet to Oxygen outlet ratio for the SSEP & Pt/CeO$_2$ catalyst.](image)

The minor error of these ratios may be due to errors in the experimental measurements. In this regard, the precision of the experimental results is acceptable.

It is very difficult to find an experiment described in literature with completely matched parameters including type of fuel, water/carbon ratio, flow rate, pressure, and temperature. It seems that for any catalyst, there is an optimal set of parameters
and, that researcher try to use these parameters in their experimental results. Thus, a comparison between the present results and other’s results can only show where we are with respect to the performance obtained by other researches and can’t be considered as an apple-to-apple comparison like shown in Figure 4.5.

![Figure 4.5. Fuel conversions for an SSEP catalyst and an Rh-based catalyst [149].](image)

Although in the SSEP YLNCCe catalyst there is no precious metal, the performance of the SSEP YLNCCe catalyst is much better than the conversion of a reforming catalyst presented in the work by Krummenacher et al. using an Rh-containing catalyst [9].
4.2 POXR results for catalysts in absent of YSZ or LSM

In order to confirm the existence of the SSEP, YNCCe containing YSZ, Ni, Cu and CeO$_2$ without LSM and LNCCe containing LSM, Ni, Cu, and CeO$_2$ without YSZ were synthesized and evaluated in the POX reforming reactor (Table 4.2).

Table 4.2. Composition of SSEP catalyst YLNCCe and two catalysts missing YSZ or LSM.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>YSZ, wt%</th>
<th>LSM, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>Ce, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YLNCCe</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>LNCCe</td>
<td>0.0</td>
<td>80</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>YNCCe</td>
<td>80</td>
<td>0.0</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

In the catalyst list, Y=YSZ, L=LSM, N=Ni, C=Cu, Ce=CeO$_2$

From Figure 4.6 and Figure 4.7, it is easy to see the outstanding performance of the YLNCCe catalyst, especially when compared to the performance of YNCCe or LNCCe catalysts. The YLNCCe catalyst shows near-100 % fuel conversion, even at temperatures as low as 450 °C.
More importantly, the yield of $\text{H}_2+\text{CO}$ for the YLNCCe catalyst was actually measureable, around 20%, at this low temperature.

Figure 4.6. Fuel conversions of SSEP catalyst YLNCCe, LNCCe without YSZ and YNCCe without LSM.

Compare that to virtually zero yield of synthesis gas for the other two catalysts on the temperature range 450-500 °C. At higher temperatures, around 650 °C, the
YLNCCe catalyst boasts a yield of over 90%. Combining the fuel conversion and yield performance, the performance of the YLNCCe catalyst is much better than that of the other two kinds of catalysts especially at the low temperatures 450 °C and 500 °C.

4.3 Discussion

![Figure 4.8. Fuel conversions and yield of H₂+CO for SSEP catalyst versus non-SSEP LNCCe without YSZ and YNCCe without LSM at 450 °C.](image)

As shown in Figure 4.1 and Figure 4.2, the POX reforming performance of YLNCCe catalysts is better than that of the commercial catalyst, Pt/CeO₂, under the same operation conditions. This extraordinarily high and unprecedented performance by itself is difficult to be explained with other mechanisms, but
self-sustained electrochemical promotion. This can be verified by comparing the catalytic POX reforming results for catalyst YLNCCe to YNCCe (without LSM), and LNCCe (without YSZ). The performance results at the 450 °C and 500 °C for the three catalysts in the Table 4.2 were re-plotted in Figure 4.8 and Figure 4.9.

![Figure 4.9. Fuel conversions and yield of H₂+CO for SSEP catalysts versus non-SSEP LNCCe without YSZ and YNCCe without LSM at 500 °C.](image)

From Figure 4.8, at 450 °C the fuel conversion for both YNCCe and LNCCe catalysts are 28.6% and 25.0% respectively while the yield of H₂ and CO are 0.12% and 0.0% respectively. Thus, the summation of the fuel conversions for YNCCe
LNCCe is 53.6% while the summation of the yields is 0.62%. Both values are much lower than those for YLNCCe containing YSZ, LSM, Ni, Cu, and CeO₂. Similar observations can be found for the results obtained at 500 °C, from Figure 4.9. In other words, if the YSZ and LSM are combined together by adding YSZ to LNCCe or LSM to YNCCe, the performance of the YNCCe and LNCCe can be significantly increased up to 100-fold! This is a typical phenomenon in which one plus one can be much greater than two. In addition, the performance of this combined YLNCCe is much better than precious metal-based catalysts. This is very unlikely to be explained by the formation of a new and very effective material during catalyst synthesis, metal-support interactions, specific surface area, and so on. However, if one evokes the concepts of electrochemical promotion and SSEP that were described in the previous chapters, the phenomenon is easy to explain. Experimental results clearly reveal that the absence of the oxygen ion conductors or cathode phases does result in a significant reduction of the performance. This indicates that coupling between the anode and cathode phases via the oxygen ion conductor is the key for the observed outstanding performance of the SSEP catalysts.

In order to further confirm the mechanism of SSEP, the specific surface area
and XRD for these catalysts were conducted. As expected, the specific surface area of the prepared catalyst is much lower than that of the precious metal catalysts including the commercial precious metal catalyst Pt/CeO$_2$ (99 m$^2$/g) and Rh based catalyst (10 m$^2$/g) [150] as shown in Table 4.3. This eliminates the possibility that the very high performance of the YLNCCe catalyst is due to its high specific surface area.

<table>
<thead>
<tr>
<th>Name</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YLNCCe catalysts</td>
<td>5.0</td>
</tr>
<tr>
<td>YNCCe catalysts</td>
<td>2.0</td>
</tr>
<tr>
<td>LNCCe catalysts</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt/CeO$_2$</td>
<td>99</td>
</tr>
<tr>
<td>Rh based catalysts</td>
<td>10</td>
</tr>
</tbody>
</table>

As shown in Figure 4.10, the XRD patterns of three different kinds of catalysts YLNCCe, YNCCe and LNCCe suggest that each of the phases can be identified as expected, e.g. the five signature peaks of YSZ at 2θ values of 30.10°, 34.89°, 50.21°, 59.79° and 62.59° [145] are shown in the XRD spectrum. The peak of Ni and Cu is overlap, when the catalysts contain both element Ni and element Cu. The mixed peak of Ni and Cu is moved to the midpoint of the individual peaks of Ni and Cu. Thus, there is no new compound or new material produced during the preparation.
process. This eliminates the possibility that the very high performance of the YLNCCe is due to formation of certain new material.

Figure 4.10. XRD spectra of catalyst YLNCCe, LNCCe and YNCCe.

4.4 Summary

The SSEP catalysts were synthesized via the preparation process shown in Figure 3.1. The performance of the SSEP catalysts was compared with the precious metal catalysts including the commercial precious metal catalyst, Pt/CeO$_2$ and Rh based catalysts. In addition, in order to confirm the existence of the SSEP, YNCCe catalyst without LSM and LNCCe catalyst without YSZ were synthesis and evaluated. The characteristic properties of all these catalysts were studied by SEM, EDS, XRD and
BET specific surface area. The reforming experimental results show that the performance of the newly developed SSEP catalysts is much better than that of the precious metal catalysts. By the comparison between YLNCCe, YNCCe and LNCCe, it is clear that the only reasonable explanation for the high performance is the self-sustained electrochemical promotion or SSEP in the catalyst. This conclusion is further verified by the results of XRD and specific surface area analyses.
CHAPTER 5 EFFECTS OF EXPERIMENTAL AND CATALYTIC PARAMETERS

In this chapter, firstly, experimental results for the effects of the flow rate and pressure on the catalyst performance are presented. Secondly, the effect of each component in the SSEP catalysts is analyzed. Thirdly, SEM, EDS and TEM studies of the structure and morphology of the catalysts are summarized. Finally, the effect of the composition in the SSEP catalyst is evaluated and explained by a theory of electrochemical promotion proposed by Vayenas [181].

5.1 Effect of the experimental parameters

5.1.1 Effect of the flow rate

As shown in Figure 5.1, the yield of H₂ and CO varies with flow rate of air. The yield of H₂ and CO decrease as a function of temperature at 550 °C. At a specific temperature above this, the flow rate of air still needs to be adjusted to obtain the optimal performance. As for the catalyst YSZ/LSM/Cu/Ni/Ce, the optimal flow rates of air are 100 mL/min, 200 mL/min, and 200 mL/min for 550 °C, 600 °C and 650 °C, respectively.

Because the reforming reaction rate increases as a function of temperature, at a
higher temperature and faster flow rate of air, more O\(_2\) is required to completely convert fuel into the H\(_2\) and CO.

![Figure 5.1. Effect of flow rate on the yield of H\(_2\) and CO at different temperatures.](image)

**5.1.2 Effect of the pressure**

As shown in Figure 5.2, pressure of air at the inlet is another important factor for the performance of the catalyst. The yield of H\(_2\) and CO was about 72.9 %, 84.98 %, and 63.9 % at 3 psig, 5 psig, and 12 psig, respectively. At any temperature, low pressure of air leads to an insufficient supply of O\(_2\) for reforming and hence a low yield of useful gases (H\(_2\)+CO). However, high pressure of air means an excess supply of O\(_2\) into the reactor. This results in an over-oxidation of carbon from CO to
CO₂ and hence reduces the yield of useful gases. Therefore, it’s very important to implement an optimal pressure at a given temperature for the reforming.

![Figure 5.2](image1.png)

**Figure 5.2.** Effect of pressure on the yield of H₂+CO at 600 °C.

![Figure 5.3](image2.png)

**Figure 5.3.** Ratio of yield of H₂+CO versus C/O at 600°C.

The average ratio of C/O was 0.72, as can be seen from the Figure 5.2. This served to balance the O₂ reformation with the carbon monoxide/dioxide oxidation.
5.2 Effect of each component in the SSEP catalysts

5.2.1 Catalytic performance for the catalysts

In order to evaluate the effect of each component in the SSEP YLNCCe catalysts, a series of experiments were conducted to test the catalysts with or without a component or components. The compositions of the various catalysts used in this experiment are listed in Table 5.1.

Table 5.1. Compositions of YSZ-based catalysts with missing components.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>YSZ, wt%</th>
<th>LSM, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>Ce, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YLNCCe</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>YLNCe</td>
<td>40</td>
<td>40</td>
<td>16</td>
<td>0.0</td>
<td>4.0</td>
</tr>
<tr>
<td>YLCCe</td>
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<td>40</td>
<td>0.0</td>
<td>16</td>
<td>4.0</td>
</tr>
<tr>
<td>LNCCe</td>
<td>0.0</td>
<td>80</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>YNCCe</td>
<td>80</td>
<td>0.0</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>YSZ Ni</td>
<td>84</td>
<td>0.0</td>
<td>16</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

In order to confirm the existence of the SSEP, YNCCe containing YSZ, Ni, Cu and CeO$_2$ without LSM and LNCCe containing LSM, Ni, Cu, and CeO$_2$ without YSZ were synthesized and evaluated in the POX reforming reactor. These results are used as a baseline (reference) for this group of tests. There are absent components in other catalysts. For example, the second catalyst does not contain Cu and the third catalyst does not contain YSZ.
Figure 5.4 presents the conversion of the catalysts as a function of temperature.

All catalysts that do not include one or more components yield a lower conversion than the one with all components (YLNCCe).

![Graph showing fuel conversion vs. temperature for SSEP & catalysts lacking one or more components.](image)

Figure 5.4. Fuel conversion vs. temperature for SSEP & catalysts lacking one or more components.

When the oxygen ion conductor (YSZ) or the cathode material (LSM) is absent, the conversion is significantly lower than that for catalysts with a complete set of the components in an SSEP catalyst. The yield of H$_2$+CO as a function of temperature is shown in the Figure 5.5. Similar to the fuel conversion, the SSEP YLNCCe catalyst has the best performance in this group of catalysts. Without an oxygen ion conductor (YSZ) or a mixed conductor (LSM), a decrease in the yield of H$_2$+CO is
significant. This difference can’t be explained by a difference in the total amount of Ni and Cu because LNCCe, YSZ Ni, and YNCCe contain the same amount of Ni and Cu. The absence of Cu has the most minimal effect on the SSEP catalysts.

![Graph of Yield of H₂+CO vs. temperature for SSEP & catalysts lacking one or more components.](image)

**Figure 5.5.** Yield of H₂+CO vs. temperature for SSEP & catalysts lacking one or more components.

### 5.2.2 Characterization

#### 5.2.2.1 SEM analysis

From the SEM photos of the catalyst YLNCe shown in Figure 5.6, they reveal that the catalyst YLNCe is kind of porous-structured catalyst.
The pore size ranges from sizes of 500 nm to 2 µm. After the reforming process, these pores tend to disappear.

Figure 5.6. SEM of catalyst YLNCe before (a) and after (b) reforming.

Catalyst YLCCe before and after reforming was examined using SEM. As shown in Figure 5.7 (a), the catalyst YLCCe is a porous structure and part of the copper
coked together. Figure 5.7 (b) easily shows that the catalyst has a serious carbon deposition problem after reforming.

Figure 5.7. SEM images of catalyst YLCCe (a) before & (b) after reforming.

SEM micrographs of the LNCCe catalyst (a) before, and (b) after reforming are shown in Figure 5.8. In comparison with catalyst before reforming, the catalyst after
reforming is subject to some serious carbon deposition problems, which block the reactor.

Figure 5.8. SEM images of catalyst LNCCe (a) before & (b) after reforming.

Catalyst YNCCe was examined using SEM and shown in Figure 5.9. In comparison with catalyst before reforming, the catalyst after reforming has serious
carbon deposition, much like the last catalyst examined under the SEM, the LNCCe catalyst.

Figure 5.9. SEM images of catalyst YNCCe (a) before & (b) after reforming.

Catalyst YSZ Ni was examined using SEM and shown in Figure 5.10. The size of the Ni particles is about 100 nm. This kind of catalyst also has a typically porous
structure. The pore size is 300 nm-500 nm. However, the carbon deposition occurred on this one during the reforming process as well.

![Figure 5.10. SEM images of catalyst YSZ/Ni (a) before & (b) after reforming.](image)

Figure 5.10. SEM images of catalyst YSZ/Ni (a) before & (b) after reforming.

From the preceding set of micrographs it should be clear that SSEP catalysts function best with the proper proportions of all five ingredients.
5.2.2.2 EDS analysis

Figure 5.11 is the EDS of the catalyst YLNCe. It clearly shows that there is no element Cu peak in this catalyst. It only includes the peaks of YSZ, LSM, Ni and ceria. Table 5.2 lists the compositions from the YLNCe catalysts evaluations using the EDS analyses at one area and four spots. It clearly shows the entire element as expected. However, the component phases cannot be completely pin-pointed.

![Figure 5.11. EDS of the catalysts containing YSZ, LSM, Ni, and Ce.](image)

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
<th>Pt</th>
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<td>0.00</td>
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<td>10.29</td>
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<td>44.50</td>
<td>0.00</td>
<td>10.61</td>
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</tr>
<tr>
<td>Point 2</td>
<td>14.34</td>
<td>43.22</td>
<td>0.00</td>
<td>9.47</td>
<td>4.76</td>
<td>28.22</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 3</td>
<td>15.65</td>
<td>21.79</td>
<td>0.00</td>
<td>0.00</td>
<td>0.17</td>
<td>10.20</td>
<td>27.22</td>
<td>24.98</td>
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<td>0.00</td>
</tr>
<tr>
<td>Point 4</td>
<td>5.81</td>
<td>57.85</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>13.09</td>
<td>1.53</td>
<td>21.72</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The EDS results of YLCCe are shown in Figure 5.12 and Table 5.3. All the elements are identified as expected. It includes YSZ, LSM, Cu and ceria. This
catalyst does not contain the element Ni. Table 5.3 lists the compositions from YLCCe evaluations using the EDS analyses at one area and four spots.

Figure 5.12. EDS of the catalysts containing YSZ, LSM, Cu and CeO₂.

Table 5.3. Element weight concentrations from EDS tests on catalyst YLCCe.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
<th>Pt</th>
</tr>
</thead>
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<td>37.34</td>
<td>3.77</td>
<td>8.21</td>
<td>16.52</td>
<td>21.44</td>
<td>5.39</td>
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<td>0.00</td>
</tr>
<tr>
<td>Point 1</td>
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<td>0.00</td>
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<td>6.12</td>
<td>16.60</td>
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<td>2.93</td>
<td>23.67</td>
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</tr>
<tr>
<td>Point 2</td>
<td>16.04</td>
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<td>7.53</td>
<td>7.56</td>
<td>5.11</td>
<td>19.82</td>
<td>38.53</td>
<td>5.41</td>
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<td>Point 3</td>
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<td>0.00</td>
<td>0.81</td>
<td>0.96</td>
<td>4.26</td>
<td>0.00</td>
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</tr>
<tr>
<td>Point 4</td>
<td>10.43</td>
<td>0.00</td>
<td>11.20</td>
<td>5.05</td>
<td>2.25</td>
<td>20.14</td>
<td>30.51</td>
<td>20.41</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The EDS was also conducted on the LNCCe catalyst. The results are shown in Figure 5.13 and Table 5.4. The results indicate that the catalyst contains LSM, Ni, Cu, ceria and doesn’t contain YSZ.
The component phases cannot be completely pinpointed. All the spot EDS analysis results show presence of all elements.

![Figure 5.13. EDS of the catalysts containing, LSM, Ni, Cu, and CeO$_2$.](image)

Table 5.4. Elemental weight concentrations from EDS tests on catalyst LNCCe.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
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<td>0.00</td>
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<td>0.00</td>
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</tr>
<tr>
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<td>0.00</td>
<td>62.76</td>
<td>0.56</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 2</td>
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<td>7.38</td>
<td>9.28</td>
<td>0.00</td>
<td>0.00</td>
<td>59.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 3</td>
<td>5.25</td>
<td>40.38</td>
<td>36.58</td>
<td>1.06</td>
<td>0.00</td>
<td>0.00</td>
<td>13.67</td>
<td>3.05</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 4</td>
<td>14.81</td>
<td>15.20</td>
<td>11.76</td>
<td>1.77</td>
<td>0.00</td>
<td>0.00</td>
<td>50.15</td>
<td>6.31</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

EDS analyses were conducted on one area and four spots on the catalyst YNCe. The results are listed in Table 5.5.
The data show that the catalyst YNCCe contains the entire elements, whereas the component phases cannot be completely pin-pointed or separated out. Only the peaks of YSZ, Ni, Cu and ceria can be found in the EDS shown in Figure 5.14.

![Figure 5.14. EDS of the catalysts containing YSZ, Ni, Cu, and Ce.](image)

Table 5.5. Element weight concentrations from EDS tests on catalyst YNCCe.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
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<tr>
<td>Point 2</td>
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<td>Point 4</td>
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<td>0.00</td>
<td>5.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 5.15 shows the EDS analysis of YSZ-Ni and the resulting peaks of YSZ and Ni, with no extra peaks. The EDS results are listed in the Table 5.6. It indicates that this catalyst only includes YSZ and Ni.
The EDS results confirm the statement that creating these catalysts does not involve making new materials, as in a chemical reaction combining Y and Ni, say.

Figure 5.15. EDS of the catalysts containing YSZ and Ni.

Table 5.6. Element weight concentrations from EDS tests on YSZ Ni powder.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
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<th>Ce</th>
<th>Gd</th>
<th>Pt</th>
</tr>
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<tbody>
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<td>23.98</td>
<td>0.00</td>
<td>0.00</td>
<td>15.56</td>
<td>60.46</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 1</td>
<td>0.00</td>
<td>33.73</td>
<td>0.00</td>
<td>0.00</td>
<td>21.09</td>
<td>45.18</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 2</td>
<td>0.00</td>
<td>41.56</td>
<td>0.00</td>
<td>0.00</td>
<td>17.72</td>
<td>40.72</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 3</td>
<td>0.00</td>
<td>34.70</td>
<td>0.00</td>
<td>0.00</td>
<td>19.49</td>
<td>45.81</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 4</td>
<td>0.00</td>
<td>41.40</td>
<td>0.00</td>
<td>0.00</td>
<td>19.29</td>
<td>39.31</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

5.3 Discussion

5.3.1 Role of the LSM in the SSEP catalyst

LSM does not have catalytic activity for hydrocarbon reforming. However, LSM is selected as the cathode for SSEP catalysts, because of its high catalytic activity of oxygen reduction [151, 152]. It can continually and quickly supply
oxygen ion to the reforming reactions. Without LSM, the only way to get the necessary oxygen ions is through the adsorption of the oxygen from the air by the YSZ. This chemical process is much slower than the electrochemical process of oxygen reduction on the LSM. Therefore, absent oxygen ions significantly impact the performance of the catalysts in a negative way.

5.3.2 Effect of the CeO$_2$ in the SSEP catalyst

Cerium dioxide (CeO$_2$), or ceria, is a promising material that has potential for a number of applications, e.g. ceramics, fuel cell, gas sensors, solid electrolyte and ceramic biomaterials. Particularly, the presence of CeO$_2$ in various catalyst systems has been found to be effective in the promotion of catalytic reactions for CO$_2$ activation, CO oxidation, CO/NO removal, and catalytic combustion of CH$_4$ [153-155]. There are different explanations for the effect of the CeO$_2$ or ceria.

1) The first is related to the fact that ceria has oxygen storage and release capacity (OSC) via the redox shift between Ce$^{4+}$/Ce$^{3+}$ under oxidizing and reducing conditions, respectively [156-162]. By adding CeO$_2$ to the catalyst system, the carbon deposition can be suppressed.
2) The second explanation was proposed by Gorte and his coworkers. In a system containing Cu-Ni alloy and ceria, ceria is a catalyst for the oxidation of hydrocarbons and may also assist in charge transfer at the interface, while Cu-Ni alloy acts primarily as an electronic conductor [169-171]. They found that a relatively small amount of ceria, only about 2 vol%, was required to enhance activity. It has been shown the addition of more ceria does not enhance performance beyond what is obtained with a minimal amount [171,172].

3) The third explanation is that CeO$_2$ can act as a structure promoter for a catalyst. Addition of CeO$_2$ promotes dispersion of the active metal catalyst [163].

4) Finally, presence of ceria in a catalyst system could enhance the steam and propane adsorption on both metal catalyst and ceria [164].

Based on the above explanations about the effect of ceria and the experimental results obtained in this research, it is envisioned that ceria in a SSEP catalyst may have two other effects.
1) Ce/CeO$_2$ is added as an electronic promoter for the SSEP catalysts. Ce/CeO$_2$ may cover the surface of the Ni/Cu in the form of Ce$^{4+}$/Ce$^{3+}$ in an environment containing both reducing (hydrocarbons) and oxidizing (oxygen) agents and form a double layer. The double layer can change the work function and chemisorptive property. This theory helps to explain Gorte’s observation that ceria enhances the catalytic activity of Ni-Cu alloy and only 2% of ceria is required to enhance the activity.

2) As shown in the preparation process for the SSEP catalysts, the SSEP catalysts support is prepared first, then the Ni/Cu/CeO$_2$ are deposited on this support. Half of Ni/Cu/CeO$_2$ deposit on the surface of cathode material (e.g. LSM). Due to the negligible oxygen ion conductivity of LSM, the anodic catalysts deposited on the cathode have much lower activity than the anodic catalysts deposited on the oxygen ion conductor (YSZ). Adding CeO$_2$ which actually shows an oxygen ion conductivity of about 10$^{-6}$ S/cm at 600 °C may help transport the oxygen ions from LSM to the anode. However, because the oxygen ion conductivity of YSZ is in the level of 10$^{-3}$ S/cm, the
effect of ceria as an oxygen ion conductor is not comparable with that of YSZ. This also explains why the performance of the LNCCe is better than that of the YNCCe as shown in Figures 5.4 and 5.5 but much less than that for YLNCCe, the catalyst containing both YSZ and LSM.

In summary, the major effect of ceria is to improve the catalytic activity of Ni-Cu alloy as the anode catalyst in the SSEP catalysts.

5.3.3 Effect of the Ni and Cu in the SSEP catalyst

Experimental results shown in Figure 4.6 and Figure 4.7 about YLNCe (with Ni but without Cu) and YLCCe (with Cu but without Ni) indicate that absence of Cu or Ni has a minimum effect on the SSEP catalysts. The reason is that both Cu and Ni are good electron conductors [173]. Without Cu, part of the Ni can act as electron conductor. Similarly, without Ni, Cu can act as the electron conductor. Conventionally, Ni is used as the anode; however, Ni is a kind of catalyst possessing traits favorable for carbon formation. This kind of catalyst is easily deactivated. Some researcher used Cu to substitute Ni as an anode [165, 166]. This fact demonstrates that carbon formation at the anode is greatly suppressed when Ni is replaced by Cu. Unlike Ni, Cu is a poor catalyst for C-C formation. Unfortunately, Cu is also a poor catalyst for C-H and C-C
bond scission. The best performance can only be obtained by combining the Ni and Cu [157, 197-204].

5.4 Effect of the composition in the SSEP catalysts

5.4.1 Effect of the ratio of YSZ to LSM

To determine the effect of the concentration of the catalyst support, a series of SSEP catalysts with varying amounts of YSZ and LSM were evaluated by POX reforming tests. The concentrations of the catalysts are summarized in the following table.

Table 5.7. SSEP catalysts with varying concentrations of the YSZ/LSM support.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>YSZ, wt%</th>
<th>LSM, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>Ce, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YLNCCe¹</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>1YLNCCe</td>
<td>60</td>
<td>20</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>YNCCe</td>
<td>80</td>
<td>0.0</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Figure 5.16 shows that fuel conversion increases as a function of the temperature. The fuel conversion of YLNCCe is almost 100% fuel conversion in the full range of temperatures from 450 to 650 °C, while the fuel conversion of 1YLNCCe decreases sharply below 600 °C.
The fuel conversion of YNCCe is between those of YLNCCe and 1YLNCCe from 450 to 500 °C, but is still low.

Figure 5.16. Fuel conversions for catalyst with varying concentration 40% LSM for YNCCe, 20% LSM for 1YLNCCe and 0.0% LSM for YNCCe.

Figure 5.17 gives the yields of these three different kinds of catalysts. The yield of H₂ and CO for YLNCCe is about 20.0 % at 450 °C, and around 87 % at 600 °C. Those for 1YLNCCe and YNCCe are practically nil at 450 °C. At 600°C, the yield is 50% for 1YLNCCe or about 2% for YNCCe.
Strong evidence suggests that at temperatures above 650 °C, the SSEP catalyst YLNCCe predictably approaches an H$_2$ + CO yield of over 90%.

Figure 5.17. Yield of H$_2$ and CO for YLNCCe catalysts of varying concentrations 40% LSM for YNCCe, 20% LSM for 1YLNCCe and 0.0% LSM for YNCCe.

5.4.2 Effect of mass ratio of Ni-Cu to the support

From the POX reforming results in section 5.4.1, it is clearly shown that the best performance of the SSEP catalysts can only be obtained around at 1:1 ratio of YSZ to LSM.
It's now necessary to study the effect of amount of Ni-Cu versus amount of support. The POX reforming tests were conducted on a series of catalysts listed in the following table, Table 5.8.

Table 5.8. SSEP catalysts with varying amounts of anode.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>YSZ, wt%</th>
<th>LSM, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>Ce, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2YLNCCe</td>
<td>44</td>
<td>44</td>
<td>2.8</td>
<td>2.9</td>
<td>6.3</td>
</tr>
<tr>
<td>3YLNCCe</td>
<td>40</td>
<td>40</td>
<td>4.5</td>
<td>4.8</td>
<td>10.7</td>
</tr>
<tr>
<td>YLNCCe</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>4YLNCCe</td>
<td>34</td>
<td>34</td>
<td>13</td>
<td>13</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Figure 5.18 shows that the yield of $\text{H}_2+\text{CO}$ for YLNCCe is again the best.

![Figure 5.18. Yield of $\text{H}_2+\text{CO}$ as functions of temperature for SSEP catalysts.](image)

Other SSEP catalysts listed in Table 5.8 have lower yields of $\text{H}_2+\text{CO}$. In terms of yield of $\text{H}_2+\text{CO}$, the best ratio of Ni-Cu to support is 0.2.
Figure 5.19 confirms that the catalyst YLNCCe again yields the highest fuel conversion. The conversion of the SSEP catalysts increases when the concentration of Ni-Cu alloy increases from 5.7 % & 9.3 %, to 16 %. However, the fuel conversion of the SSEP catalysts decreases when the concentration of the Ni-Cu is increased from 16 % to 26 %.

![Graph showing fuel conversions as functions of temperature for SSEP catalysts.](image)

Figure 5.19. Fuel conversions as functions of temperature for SSEP catalysts.

5.5 Characterization

5.5.1 Specific surface area-BET analysis

The specific surface areas of YSZ/LSM supports and YLNCCe were evaluated by the ASAP 2020 at Florida State University, and are listed in Table 5.9.
Similarly, Figure 5.20 (a) shows a surface image of the porous support YSZ/LSM prepared by the method illustrated in Figure 3.1.

Table 5.9. Specific surface area of the support and catalysts.

<table>
<thead>
<tr>
<th>Name</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ/LSM (1:1) support</td>
<td>0.5</td>
</tr>
<tr>
<td>YLNCCe (1:1) catalysts</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The image shows that the support has many micro-pores, which were caused by the evaporation of graphite and polymethyl-methacrylate (PMMA) during the sintering step in the preparation process. The size of the pores ranges from 25 nm to 600 nm. Figure 5.20 (b) displays the image of a catalyst containing Ni, Cu and Ce (8 wt% Ni, 8 wt% Cu and 3.4 wt% Ce) which was loaded to the support surface by the
impregnation method and then reduced in H₂ for 2 hours at 520 °C. It shows that the Ni, Cu, and ceria uniformly cover the framework of the support.

Figure 5.20. SEM images of (a) support YSZ/LSM & (b) SSEP YLNCCe catalyst.

The YSZ/LSM support cross-section was also examined by the SEM. The SEM photograph in Figure 5.21 clearly displays the porous structure of the supports. The pore size for the support YSZ/LSM ranges from 25 nm to 600 nm. However, its specific surface area value (0.5 m²/g) suggests that it is not typically a highly porous material.
Figure 5.21 also indicates that there are two different level channels: the ones less than 20 nm are considered small channels whereas ones 300 nm or larger are main channels.

Likewise, the commercial catalyst Pt/CeO$_2$ before and after reforming were examined by SEM and shown in Figure 5.22.
Figure 5.22 (a) shows the SEM micrograph of the catalyst Pt/CeO$_2$ before reforming. It is also a kind of porous structure.

Figure 5.22. SEM images of commercial Pt/CeO$_2$ (a) before & (b) after reforming.

The SEM photographs in Figure 5.23 were taken on the surface of the (a) YSZ/LSM (3:1) support and the (b) 1YLNCCe catalyst on this support. Figure 5.23
(a) clearly shows that the support is a porous structure. In Figure 5.23 (b), after impregnation and reduction, the catalyst based on this support is still a porous structure. Thus, the Ni, Cu and ceria have been deposited on the surface of the support very well.

Figure 5.23. SEM images of (a) 3:1 YSZ/LSM & (b) SSEP 1YLNCCe catalyst.
5.5.2 EDS analysis

EDS tests were conducted on the catalysts, and the tests included both area tests and point tests. Figure 5.24 is the EDS for YLNCCe catalyst. The EDS results for YSZ/LSM and YLNCCe are listed respectively in Table 5.10 and Table 5.11.

Figure 5.24. SEM images of (a) support YSZ/LSM & (b) SSEP YLNCCe catalyst.

Table 5.10. Elemental weight concentration % obtained from EDS measurements at one area and two spots on the YSZ, LSM support.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>One area</td>
<td>15.46</td>
<td>0.00</td>
<td>0.00</td>
<td>8.07</td>
<td>8.98</td>
<td>31.63</td>
<td>35.86</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 1</td>
<td>17.90</td>
<td>0.00</td>
<td>0.00</td>
<td>2.58</td>
<td>9.66</td>
<td>25.66</td>
<td>44.20</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 2</td>
<td>19.86</td>
<td>0.00</td>
<td>0.00</td>
<td>3.95</td>
<td>11.81</td>
<td>21.80</td>
<td>42.59</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The data in these tables indicate that the catalyst YLNCCe contains the entire set of relevant elements, no new ones. However, the component phases cannot be completely pin-pointed, because the beam affected zone is roughly a sphere of one micrometer and hence spatial resolution of the EDS is not sufficient to allow the
pin-pointing of all the particles. Nevertheless, it’s clear that as for point 1, the element Ni and Cu are the dominant components. Thus, point 1 is considered the anode phase.

Similarly, point 2 is considered as a YSZ-dominant spot.

Table 5.11. Elemental weight concentration % obtained from EDS measurements at one area and two spots on the YLNCCe catalyst containing YSZ, LSM, Ni, Cu, and CeO$_2$.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>27.90</td>
<td>3.58</td>
<td>0.34</td>
<td>1.54</td>
<td>3.04</td>
<td>6.04</td>
<td>57.51</td>
<td>0.06</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 1</td>
<td>2.65</td>
<td>42.48</td>
<td>29.45</td>
<td>2.83</td>
<td>0.75</td>
<td>7.90</td>
<td>8.88</td>
<td>5.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 2</td>
<td>0.25</td>
<td>5.15</td>
<td>17.45</td>
<td>9.76</td>
<td>16.68</td>
<td>47.05</td>
<td>0.45</td>
<td>3.21</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The area EDS (Figure 5.25) analysis for Pt/CeO$_2$ catalyst clearly shows all elements in the catalyst.

Figure 5.25. EDS of the catalysts containing Pt and CeO$_2$.

EDS analyses were also recorded at four spots, as listed in Table 5.12. Because the beam affected zone is roughly the size of a spherical micrometer, the spatial...
resolution of the EDS is not sufficient to allow a pin-pointing of Pt and ceria particles on the surface of the catalyst support. Thus, the EDS analyses show that the concentrations for Pt and Ce do not change significantly.

Table 5.12. Element weight concentrations from EDS tests on Pt/CeO$_2$ catalyst.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>74.43</td>
<td>0.00</td>
<td>25.57</td>
<td></td>
</tr>
<tr>
<td>Point 1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>72.89</td>
<td>0.00</td>
<td>27.11</td>
<td></td>
</tr>
<tr>
<td>Point 2</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>74.43</td>
<td>0.00</td>
<td>25.57</td>
<td></td>
</tr>
<tr>
<td>Point 3</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>72.08</td>
<td>0.00</td>
<td>27.92</td>
<td></td>
</tr>
<tr>
<td>Point 4</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>77.60</td>
<td>0.00</td>
<td>22.40</td>
<td></td>
</tr>
</tbody>
</table>

The EDS of YLNCCe 1:1 catalysts shown in Figure 5.26 indicates that it includes YSZ, LSM, Cu, Ni and ceria.

![EDS of SSEP YLNCCe 1:1 catalyst](image)

Figure 5.26. EDS of the SSEP YLNCCe 1:1 catalyst.

The percentages of atomic weight for the elements in YLNCCe (1:1) catalysts are listed in Table 5.13. This data shows that the catalyst YLNCCe contains the entire set
of relevant elements. However, the component phases cannot be completely pin-pointed or singled out. It’s also clear that as for Point 3 in Table 5.12, zirconia and yttrium are the dominant components, so point 3 is considered the electrolyte phase. Similarly, point 1 is considered the cathode phase. Point 2 is the anode phase.

![Figure 5.27. EDS of the SSEP YLNCCe 3:1 catalyst.](image)

As for the EDS of 1YLNCCe (with YSZ to LSM 3:1) catalyst, shown in Figure 5.27, all the expected elements are identified. However, in this spectrum the ratio between the YSZ and LSM is changed.
Comparing Figure 5.27 to Figure 5.26, the amount of LSM is decreased in the YLNCCe 3:1 catalyst, as can be inferred by the relative shrink of the La and Mn peaks.

Table 5.13. Element weight concentrations from EDS tests on YLNCCe catalyst

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>27.90</td>
<td>3.58</td>
<td>0.34</td>
<td>1.54</td>
<td>3.04</td>
<td>6.04</td>
<td>57.51</td>
<td>0.06</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 1</td>
<td>27.69</td>
<td>5.15</td>
<td>4.90</td>
<td>5.23</td>
<td>0.00</td>
<td>0.00</td>
<td>57.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 2</td>
<td>2.65</td>
<td>42.48</td>
<td>29.45</td>
<td>2.83</td>
<td>0.75</td>
<td>7.90</td>
<td>8.88</td>
<td>5.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 3</td>
<td>0.25</td>
<td>5.15</td>
<td>17.45</td>
<td>9.76</td>
<td>16.68</td>
<td>47.05</td>
<td>0.45</td>
<td>3.21</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

5.5.3 TEM analysis

Figure 5.28. TEM images of the YSZ/LSM support.

Figure 5.28 is a TEM image of the support YSZ/LSM. It clearly shows that the support is a kind of porous structure. The pore size for this support is about 50 nm to
200 nm, which is similar to the SEM examined result in order of magnitude. Figure 5.29 shows a pair of TEM images of the SSEP YLNCCe catalyst.

Figure 5.29. TEM images of SSEP YLNCCe catalyst.

The black points on the surface are the Ni, Cu and ceria, which are deposited on the surface by the impregnation method. As shown in Figure 5.29 (b), the Ni, Cu
and ceria are perfectly deposited on the surface of the pore. The size of these pores is about 200 nm.

5.6 Discussion

5.6.1 Mechanism of the SSEP in partial oxidation reforming

A more positive anode potential can enhance the classical double layer between the YSZ and metal catalyst. Then, more electrons are needed to keep the balance of the classical double layer. Thus, the amount of electrons on the gas exposed surface of the metal catalyst increases too, because a metal surface is an equipotential surface.

As mentioned in Chapter 2, the effective double layer is established on the gas-exposed, catalytically active electrode surface by the backspillover oxide ions and their compensating charge in the metal. Therefore, there is more oxygen ion backspillover to the gas exposed surface of the metal. Consequently, the field strength in the effective double layer is increased. The strong electric field strength can help break the reactants down into smaller molecules or atoms, leading to a greater promotion. The change of the double layer can also affect the work function of the metal catalyst.
As has been described in the introduction, the SSEP is realized via a constant supply of promoters to the surface of the anode catalysts, shifting the electrochemical potential in the positive direction. The process may be described with following reactions [146, 147]:

On anode catalysts:

\[
C_mH_n + \frac{m}{2} O_2 \leftrightarrow m CO + \frac{n}{2} H_2
\]  \hspace{1cm} (5.1)

which is a non-electrochemical or pure chemical reforming reaction and is accelerated by SSEP;

\[
C_mH_n + m O^{2-} \leftrightarrow m CO + \frac{n}{2} H_2 + 2m e^-
\]  \hspace{1cm} (5.2)

\[
CO + O^{2-} \leftrightarrow CO_2 + 4e^-
\]  \hspace{1cm} (5.3)

\[
H_2 + O^{2-} \leftrightarrow H_2O + 2e^-
\]  \hspace{1cm} (5.4)

which are anodic half reactions.

On cathode particles:

\[
O_2 + 4e^- \leftrightarrow 2O^{2-}
\]  \hspace{1cm} (5.5)

which is the cathodic half reaction.

In a general form of A+D→ Products [e.g. Reaction 5.1], where compound A is the electron acceptor or oxidizing reactant and compound D is the electron donor or
reducing reactant, the catalytic reaction rate of electrochemical promotion can be
calculated through the Equation 5.6 [146, 147]:

\[ r_{pro} = k_R \theta_A \theta_D \]  
(5.6)

where the coverage ratios of the electron donor and acceptor, \( \theta_D \) and \( \theta_A \) are given by:

\[ \theta_D = \frac{k_{DP} D \exp(\lambda_D \Pi)}{1 + k_{DP} D \exp(\lambda_D \Pi) + k_{AP} A \exp(\lambda_A \Pi)} \]  
(5.7)

\[ \theta_A = \frac{k_{AP} A \exp(\lambda_A \Pi)}{1 + k_{AP} A \exp(\lambda_A \Pi) + k_{DP} D \exp(\lambda_D \Pi)} \]  
(5.8)

Combining Equations 5.6-5.8 gives the catalytic rate, \( r \):

\[ r = \frac{k_R k_A k_{DP} D \exp(\lambda_D \Pi) \exp(\lambda_A \Pi)}{[1 + k_{DP} D \exp(\lambda_D \Pi) + k_{AP} A \exp(\lambda_A \Pi)]^2} \]  
(5.9)

In the above equations, \( \Pi = e^{\Phi_A / k_b T} \) (\( k_b \) = Boltzmann’s constant), and all
parameters are constant except \( \Phi_A \), the potential of the anode. Therefore, the catalytic
rate of electrochemical promotion can be increased by increasing the potential of the
anode.

A general discussion can be made according to the theory. First, a solid oxide
oxygen conductor with a high ionic conductivity in the temperature range (450-650°C)
definitely benefits the SSEP via reducing IR drop. Second, a highly selective cathode
results in a more positive potential of coupled anode phases and hence a greater SSEP.
Finally, a highly effective anode for hydrocarbon oxidation is also important to achieve a high baseline performance.

5.6.2 Effect of the concentration of the SSEP support

There are mainly two ways to increase the potential of the anode:

1) Decrease the IR drop between the anode and cathode.

The SSEP catalyst enables effective coupling between two half-cell electrochemical reactions. Although the close proximities (distance from 20 nm to 20 μm) between the anode and cathode phases allow efficient transportation of electrons and oxygen ions, there are still significant IR drops between anodes and cathodes.
If the IR drop can be decreased, the potential of the anode can be increased, as shown in Figure 5.30.

Figure 5.30. Increasing anode potential by lowering IR drop.

The IR drop stems from the oxygen ion conductor and the electronic conductor.

The conductivity of solid electrolytes is much lower than the conductivity of metals.

This fact is shown in Table 5.14.

Table 5.14. Comparison between electron & oxygen ion conductors.

<table>
<thead>
<tr>
<th>Name</th>
<th>Conductivity $\sigma$ (S/cm)</th>
<th>Current carrier</th>
<th>$\sigma$ (S/cm) vs T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td>$10 &lt; \sigma &lt; 10^5$</td>
<td>Electrons</td>
<td>$\sigma\downarrow$ as $T\uparrow$</td>
</tr>
<tr>
<td>Oxygen ion</td>
<td>$10^{-3} &lt; \sigma &lt; 10$</td>
<td>Ions</td>
<td>$\sigma\uparrow$ as $T\uparrow$</td>
</tr>
</tbody>
</table>

Due to the high conductivities of the electronic conductors shown in Table 5.14, the IR drops of electronic conductors is negligible, and the IR drop of the oxygen ion...
conductor dominates the IR drop. Thus, the IR drop depends on two factors: oxygen ionic conductivity of the material and distance between an anode and cathode. While the conductivity is a material constant, changing the amount of the oxygen ion conductor can increase or decrease the distance between the anode and cathode.

Figure 5.16 and Figure 5.17 show that when the total percentage of the YSZ and LSM is fixed, the best performance of the SSEP catalysts is obtained at the 1:1 ratio of YSZ to LSM.
Figure 5.16 and Figure 5.17 also show that when the amount of the YSZ is more than 40 wt%, the performance of the SSEP catalyst is decreased. The reason may be that more YSZ has to result in less LSM shown in the transition from Figure 5.31.

(b)

Figure 5.31. Schematics of the SSEP catalysts with (a) 1:1 ratio and (b) 3:1 ratio of YSZ to LSM according to SEM images.

Both schematics clearly show that when there is more YSZ than LSM the average distance between the anodes on the YSZ and the LSM cathodes increases significantly. Consequently, the potential of the anode is decreased, leading to a lower promotion and an overall worse performance of the SSEP catalyst.
The oxygen ionic conductivities, $\sigma_{ion}$, can be calculated from diffusion data with the Nernst-Einstein equation, which relates to tracer diffusivity, $D_T$, by Equation 5.10.

$$\sigma_{ion} = \frac{D_T N q_{ion}^2}{f k T}$$  

(5.10)

In Equation 5.10, $N$ is the concentration of anion sites, $q_{ion}$ is the charge of anion and $f$, the correlation factor, is assumed to be equal to 0.69, $k$ is the Boltzmann constant.

The ionic conductivity of LSM is $4 \times 10^{-8}$ S/cm at 900 °C. The ionic conductivity of YSZ is $2.5 \times 10^{-2}$ S/cm at 800 °C.

Thus, although LSM is a mixed conductor, the oxygen ionic conductivity is much lower than YSZ. Oxygen ion transport through the LSM is negligible and LSM is considered as virtually a pure electronic conductor [148, 151]. If the anode is in contact with the cathode LSM, the anode hinders activity. In other words, the anode phases which were deposited on the LSM is not as effective as those deposited on YSZ. In addition, the presence of CeO$_2$ which is an oxygen conductor with an intermediate oxygen ion conductivity ($10^{-6}$ S/cm) may give rise to certain SSEP when YSZ is absent.
2) Increase the total exchange current of the cathode

As shown in Figure 5.32, with the total exchange current at the cathode $I_{CA}$ is higher than that of points $I_{CB}$ and $I_{CA}$. The corresponding potential of the anode $E_{C}$ is higher than that of points $E_{B}$ and $E_{A}$ too.

![Figure 5.32. Increase anode potential by increasing total exchange current of cathode.](image)

Therefore, increasing the total exchange current of the cathode leads to a high potential of the anode.
As can be seen from Equation 5.11, increasing the effective specific surface area or the total exchange current density of the cathode can increase the total exchange current of the cathode.

\[ I_c = A_c \times \left( p_{O_2} \right)^c \left\{ \exp \left[ \frac{\beta_c F}{RT} (\Phi_c - E_{e,c}) \right] + \exp \left[ -\frac{I\beta_c}{RT} F(\Phi_c - E_{e,c}) \right] \right\} \] (5.11)

In Equation 5.11, \( i_{c,0} \) is exchange current densities for cathode reactions, \( A_c \) is the effective specific surface area of the Cathode, \( \Phi_c \) is the electrochemical potential of the catalysts, \( E_e \) is the electrochemical equilibrium potentials \( \beta_c \) is the symmetry factors for cathodic reactions, \( p_i \) is the partial pressure of the species, \( F \) is Faraday’s constant, and \( T \) is temperature in Kelvin.

As for the SSEP catalysts, the effective specific surface area of the cathode is related to the amount of the LSM. The exchange current density \( i_{oc} \) is determined by the property of the cathode material. Thus, adding more LSM result in a higher potential of the anode and a higher promotion. However, when the total percentage of YSZ and LSM in the catalyst is fixed, adding more LSM lead to less YSZ. As discussed in last section, the anode phases which were deposited on the LSM are not as effective as those deposited on YSZ.

If the ratio of YSZ to LSM is fixed, the total percentage of the YSZ/LSM is
changed. As shown in Figure 5.16 and Figure 5.17, lower percentages of YSZ/LSM can decrease the performance of the SSEP catalyst. The reason is that lesser amounts of YSZ lead to a higher IR drops. Lesser amounts of LSM result in a lower effective specific surface area of the cathode and a lower total exchange current of cathode. Either a higher IR drop or a lower total exchange current of the cathode can decrease the potential of the anode and obtain less promotion from the SSEP catalyst.

Therefore, in order to increase the potential of the anode, it’s necessary to balance the two factors: the IR drop of the SSEP catalyst and the total exchange current of cathode. It has been proven that the best performance of the SSEP catalysts only can be obtained at certain concentrations of their elements, which should look to balance the overall IR drop with the total exchange current of the cathode.

5.7 Summary

In this chapter, the study of the effect of the each component and the concentration in the SSEP indicates that the best performance of the SSEP catalysts can only be obtained at an optimum composition: 40 wt% YSZ, 40 wt% LSM, 8.0 wt% Ni, 8.0 wt% Cu and 4 wt% Ce. In order to get the best performance of the SSEP catalysts, it is necessary to balance two major factors: the IR drop of the SSEP catalyst
and the total exchange current of cathode. Thus, the performance of the SSEP catalyst strongly depends on the percentages of the major components, and in particular the amount of YSZ versus that of LSM and the amount of YSZ/LSM versus that of other components. In order to further improve the performance, it is necessary to replace the major components with other materials that provide better functional properties, for example, oxygen ionic conductivity for the oxygen conductor, cathodic exchange current density for the cathodes, and anodic catalytic activity for the anodes.
CHAPTER 6 REPLACEMENT OF THE SOLID ELECTROLYTE AND CATHODE MATERIAL

In Chapter 6, the SSEP catalyst is improved based on the study completed in Chapter 5. The performance of the SSEP catalyst is affected by the concentration and the best performance of the SSEP YLNCCe catalysts can only be obtained at certain concentrations. One prediction was that the performance of the SSEP catalysts would be limited by properties of component materials. In other words, the performance of the SSEP can be improved by replacing each component with materials with better functional properties such as the oxygen reduction activity for cathode and ionic conductivity for oxygen ion conductor. For example, GDC should have a greater ionic conductivity than YSZ. Therefore, GDC may be a better alternative for the oxygen ion conductor. LSCF is known to have better oxygen reduction activity. Therefore, LSCF may be a better alternative than LSM. In this chapter, new SSEP catalysts based on GDC/LSM or YSZ/LSCF are synthesized and evaluated.
6.1 Improvement of the SSEP catalyst GLNCCe

In order to study the performance of the GLNCCe catalysts and prove how to improve SSEP catalysts, three different kinds of the catalyst with the same ingredients just with different ratios, were synthesized. The first one is the GLNCCe catalyst with a smaller percentage of Ni and Cu, the second one is the GLNCCe catalyst with a higher percentage of Cu and Ni. The third one was synthesized by adding the Zn to the GLNCCe catalysts.

Table 6.1. Compositions of catalysts for the SSEP GLNCCe catalyst.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>GDC, wt%</th>
<th>LSM, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>Ce, wt%</th>
<th>Zn, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1GLNCCe</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2GLNCCe</td>
<td>40</td>
<td>40</td>
<td>5.0</td>
<td>5.0</td>
<td>10</td>
<td>0.0</td>
</tr>
<tr>
<td>GLNZCCe</td>
<td>38</td>
<td>38</td>
<td>5.0</td>
<td>5.0</td>
<td>10</td>
<td>4.0</td>
</tr>
</tbody>
</table>

6.1.1 Catalytic performance evaluation for GLNCCe

Figure 6.1 shows the yield of H\textsubscript{2}+CO for three different kinds of catalyst. The components of the catalysts are listed in Table 6.1. This table and figure set reveals the yield of H\textsubscript{2}+CO increases as a function of the temperature. The yield of H\textsubscript{2}+CO of

\footnote{Note: In the catalyst list, G=GDC, L=LSM, N=Ni, C=Cu, Ce=\textit{CeO\textsubscript{2}}, Z=Zn}
1GLNCCe is higher than that of 2GLNCCe during 450 to 650 °C. The yield of H$_2$+CO of GLNZCCe is similar to that of the 2GLNCCe between the range 550 °C and 650 °C. However, the yield of H$_2$+CO of GLNZCCe decreases significantly after 550 °C, while the hydrogen and CO are undetectable at 450 °C.

Figure 6.1. Yield of hydrogen and CO as functions of temperature.

Figure 6.2 shows the fuel conversion as a function of temperature. Above 550 °C, the fuel conversion for these three different kinds of catalyst is 100%. Below 550 °C, the fuel conversion of GLNZCCe decreases quickly. The fuel conversion of GLNZCCe was not tested below this temperature because the hydrogen and CO could
not be detected at 500 °C. The fuel conversion of GLNCCe batch 1 decreases significantly below 500 °C.

Figure 6.2. Fuel conversion as functions of temperature.

Combining yield of $\text{H}_2 + \text{CO}$ and fuel conversion, GLNCCe batch 2 (GDC wt% 40, LSM wt% 40, Ni wt% 8.0, Cu wt% 8.0, and CeO$_2$ wt% 4) has the best reforming performance. The reforming performance of GLNCCe is not improved by adding ZnO.
6.1.2 Catalytic performance comparison

Table 6.2. Compositions of SSEP catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>GDC, wt%</th>
<th>YSZ, wt%</th>
<th>LSM, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>Ce, wt%</th>
<th>Zn, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YLNCCe</td>
<td>0.0</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>GLNCCe</td>
<td>40</td>
<td>0.0</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Figure 6.3 shows the fuel conversion of the YSZ/LSM based SSEP catalyst (YLNCCe), GDC/LSM based SSEP catalyst (GLNCCe) and a commercial Pt/CeO$_2$ catalyst.

Figure 6.3. Fuel conversions vs. Temperature for two SSEP & commercial Pt/CeO$_2$ catalyst.

It is clear that the fuel conversion and yield of $\text{H}_2$ and CO for SSEP catalysts is much greater than those of the commercial Pt/CeO$_2$ catalyst at 450 and 500 °C.
Fuel conversion is close to 100 % for the YLNCCe and GLNCCe catalysts at 450 and 500 °C. However, for the Pt/CeO\textsubscript{2} catalyst, the conversion is only 10 % at 450 °C and approximately 20 % at 500 °C.

Figure 6.4. Yield of H\textsubscript{2}+CO vs. Temperature for two SSEP & commercial Pt/CeO\textsubscript{2} catalyst.

As shown in Figure 6.4, the yield of (H\textsubscript{2}+CO) is 87.1 % for SSEP GLNCCe catalysts, 90 % for SSEP YLNCCe catalyst and 81.6 % for Pt/CeO\textsubscript{2} catalyst at 650 °C. The yield of (H\textsubscript{2}+CO) is 46.3 % for SSEP GLNCCe catalysts, 19.7 % for SSEP YLNCCe catalysts, or almost 0 % for Pt/CeO\textsubscript{2} catalyst at 450 °C.
6.1.3 Characterization

6.1.3.1 Specific surface area-BET analysis

The specific surface area of each support and catalyst is evaluated by the ASAP 2020 from Florida State University, and is listed in Table 6.3.

Table 6.3. Specific surface area of the support and catalysts.

<table>
<thead>
<tr>
<th>Name</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ/LSM (1:1) support</td>
<td>0.5</td>
</tr>
<tr>
<td>GDC/LSM support</td>
<td>1.9</td>
</tr>
<tr>
<td>YLNCCe (1:1) catalysts</td>
<td>5.0</td>
</tr>
<tr>
<td>GLNCCe catalysts</td>
<td>6.6</td>
</tr>
</tbody>
</table>

6.1.3.2 Scanning electron microscope (SEM) analysis

The relationship between the composition of catalyst and its morphology could be taken from SEM pictures directly. Figure 6.5 (a) is the surface image of the porous catalyst support GDC/LSM, prepared by the casting method. The image shows the support has many micro-pores, which are formed by the evaporation of the graphite and polymethyl-methacrylate (PMMA) during the preparation process.

Figure 6.5 (b) displays the image of a synthesized catalyst.
Ni, Cu and Ce (8.0 wt% Ni, 8.0 wt% Cu and 4 wt% Ce) were added to the support surface by impregnation and then reduced in H₂ for 2 hours at 520 °C.

Figure 6.5. SEM Images of the (a) support and the (b) GLNCCe catalysts.

The cross section of the GDC/LSM support was examined by a scanning electron microscope. The SEM results indicate that the GDC/LSM support is kind
of porous structure. From the cross section, a lot of reaction channels can be found.

The size of the channel ranges from 10 nm to 500 nm.

![SEM Micrograph of GDC/LSM support section.](image)

Figure 6.6. SEM Micrograph of GDC/LSM support section.

Figure 6.7 shows the SEM photograph of GLNCCe catalyst after reforming.

Compared with the fresh catalyst, the porous structure of the GLNCCe after reforming is not found.
From experimenting, it was determined that this catalyst did not face the carbon deposition problem.

Figure 6.7. SEM of GLNCCe catalysts after reforming.

6.1.3.3 EDS analysis

The EDS results shown in Figure 6.8 reveal that the SSEP GLNCCe catalysts include the Gd, Ce, La, Sr, Mn, Ni, and Cu. These elements were present in the compounds for preparation of the catalysts.
The corresponding EDS results are listed in Tables 6.4. It’s clear that as for point 3, the elements in LSM are the dominant components.

![Figure 6.8. EDS of the GLNCCe catalyst with GDC, LSM, Ni, Cu, and CeO\textsubscript{2}.](image)

Table 6.4. Element weight concentrations from EDS tests on SSEP catalyst GLNCCe.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>6.63</td>
<td>12.80</td>
<td>12.01</td>
<td>1.72</td>
<td>0.00</td>
<td>0.00</td>
<td>16.88</td>
<td>44.34</td>
<td>5.61</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 1</td>
<td>8.93</td>
<td>28.03</td>
<td>11.71</td>
<td>0.48</td>
<td>0.00</td>
<td>0.00</td>
<td>18.87</td>
<td>28.59</td>
<td>3.39</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 2</td>
<td>10.86</td>
<td>23.90</td>
<td>12.61</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>16.82</td>
<td>30.10</td>
<td>5.68</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 3</td>
<td>21.21</td>
<td>4.10</td>
<td>8.04</td>
<td>2.71</td>
<td>0.00</td>
<td>0.00</td>
<td>45.20</td>
<td>13.43</td>
<td>5.33</td>
<td>0.00</td>
</tr>
<tr>
<td>Point 4</td>
<td>6.02</td>
<td>29.37</td>
<td>19.23</td>
<td>0.77</td>
<td>0.00</td>
<td>0.00</td>
<td>14.89</td>
<td>26.21</td>
<td>3.51</td>
<td>0.00</td>
</tr>
</tbody>
</table>

6.1.3.4 XRD analysis

Figure 6.9 indicates that the support only includes GDC and LSM without new components. As for the SSEP GLNCC catalysts, all the peaks of GDC, LSM, Ni and CeO\textsubscript{2} can be found in the XRD spectrum.
Because of the previously discussed overlap of peaks of Ni and Cu, the element Cu is not labeled.

Figure 6.9. XRD spectra of GDC/LSM support and the SSEP GLNCCe catalysts.

### 6.2 Improvement to the SSEP catalyst YLFNCCe

Table 6.5. Composition of SSEP catalyst based on YSZ/LSCF.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>YSZ, wt%</th>
<th>LSCF, wt%</th>
<th>Ni, wt%</th>
<th>Cu, wt%</th>
<th>Ce, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>YLFNCCe²</td>
<td>40</td>
<td>40</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

It was hypothesized that LSCF could potentially improve the SSEP YLNCCe catalyst.

² Note: In the catalyst list, Y=YSZ, LF=LSCF, N=Ni, C=Cu, Ce=CeO₂
6.2.1 Catalytic performance evaluation of YLFNCCe

Another POX reforming experiment was conducted on the YLFNCCe catalyst; the fuel conversion of YLFNCCe is 100% and the yield $\text{H}_2+\text{CO}$ of YLFNCCe is 90% at 650 °C. However, it only lasts about 30 minutes, then the performance of the catalyst decreased significantly. This happened because of the carbon deposition problem that both LNCCe and YNCCe faced.

Figure 6.10. Reactor is blocked by the YLFNCCe after POX reforming.

The POX reactor was almost totally blocked, as shown in Figure 6.10; the flow rate displayed on the digital micrometer is only about 8 mL/min.
6.2.2 Characterization

6.2.2.1 Specific surface area-BET analysis

Table 6.6. Specific surface area of the support and catalysts.

<table>
<thead>
<tr>
<th>Name</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YLNCCe (1:1) catalysts</td>
<td>5.0</td>
</tr>
<tr>
<td>GLNCCe catalysts</td>
<td>6.6</td>
</tr>
<tr>
<td>YLFNCCe catalysts</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The specific surface area of each support and catalyst is evaluated by the ASAP 2020 from Florida State University, and is listed in Table 6.6.

6.2.2.2 SEM analysis

![SEM micrograph](image)

(a)

Figure 6.11 (a) shows the SEM micrograph of the YSZ/LSCF support and reveals similar qualities to the other SSEP catalyst supports. It is porous as well. Despite
having a smaller specific surface area, the SSEP YLFNCCe catalyst has similar
channel sizes.

Figure 6.11. SEM micrographs of (a) YSZ/LSCF support & (b) SSEP LSFCCe.

6.2.2.3 EDS analysis

The EDS results of the SSEP catalyst YFLNCCe show all of the relevant
elements. The results can be seen in Figure 6.12.
There is some evidence that suggests LSCF interacts with YSZ in ways that form new materials, as in a chemical reaction. This hinders its catalytic performance.

![Figure 6.12. EDS of the SSEP LSFCCe catalysts.](image)

### 6.3 Discussion

As discussed in Chapter 5, the performance of the SSEP catalyst is affected by the concentration and limited by certain properties of the materials used to make the SSEP catalyst. The best performance of the SSEP catalysts only can be obtained at 40 wt% YSZ, 40 wt% LSM, 8.0 wt% Ni, 8.0 wt% Cu and 4 wt% Ce. While both IR-drop and total exchange current of cathode can affect the performance of the SSEP catalyst, when the concentration is fixed, the performance of the SSEP catalyst is only related to the conductivity of oxygen ionic conductor and the total exchange current of the cathode. In other words, the performance of the SSEP catalyst can be improved by
using new materials, such as a better oxygen ion conductor, GDC, or a new, more active cathode, LSCF.

6.3.1 Improvement of the SSEP catalyst by using GDC/LSM support

As shown in Table 6.2, both YLNCCe and GLNCCe have the best performances of the SSEP catalysts. The only difference between GLNCCe and YLNCCe is that GDC is used to substitute the YSZ. From the results shown in Figure 6.3 and Figure 6.4, the fuel conversion of GLNCCe is as high as YLNCCe. However, the yield of $\text{H}_2 + \text{CO}$ is 46.3% for GLNCCe and 19.7% for YLNCCe at 450 °C. Therefore, the performance of GLNCCe is better than that of the YLNCCe, especially at the low temperatures. The possible reasons are enumerated as follows.

6.3.1.1 Effect of the specific surface area

The BET results clearly show that the specific surface area is 5 m$^2$/g for YLNCCe catalysts and 6.6 m$^2$/g for GLNCCe catalysts. The specific surface area difference between these two catalysts can be ignored when compared to the big yielding difference of these two catalysts. That being said, the better performance of GLNCCe catalysts must be caused by another reason.
6.3.1.2 New materials

The XRD spectrum of the GLNCCe clearly shows that all the peaks of GDC, LSM, Ni, ceria as expected. The peak of Cu can’t be found due to the peak overlap between Ni and Cu. There is no extra peak appearing on this XRD spectrum. Thus, there is no new material produced during the catalyst preparation. The improvement of the performance must still be caused by another reason.

6.3.1.3 Effect of the support

![Figure 6.13. Conductivity as a function of the temperature.](image)

As mentioned, the only difference between GLNCCe and YLNCCe is the oxygen ionic conductor. The reason may be that the conductivity of YSZ is not very high,
around $10^{-5}$-$10^{-3}$ S cm$^{-1}$, in the temperature range between 400 and 650 °C [174-177], and the conductivity of GDC is about $10^{-3}$-$10^{-2}$ S cm$^{-1}$ in the same temperature range, orders of magnitude better. The conductivity of the YSZ and GDC is also measured and calculated in our lab as shown in Figure 6.13. The results reveal that the conductivity of GDC is better than that of YSZ especially at the low temperature.

As mentioned, the IR drop of the SSEP catalysts is related with conductivity of the oxygen ion conductor. The higher conductivity of the GDC can decrease the IR drop of the SSEP and increase the potential of the anode, which leads to a better yield and a better performance. In addition, the conductivity of GDC is much better than that of YSZ at the relatively low temperatures. Therefore, the advantage of the higher conductivity of GDC is more obvious at the lower temperatures and results in a significantly better performance at these temperatures.

As discussed in Chapter 5, the best performance of the SSEP catalysts only can be obtained at a certain ratio of the components. It can help explain the results that the best performance of the GLNCCe catalysts is obtained at 40 wt% GDC, 40 wt% LSM, 8.0 wt% Ni, 8.0 wt% Cu and 4 wt% Ce shown in Figure 6.1 and Figure 6.2.
6.3.2 Improvement of the SSEP catalyst by using YSZ/LSCF support

The overall cathode reaction represents the reduction of oxygen from gas phase and the subsequent transfer of the reduced species into the solid electrolyte as shown in the following equation:

$$\frac{1}{2} \text{O}_2 \text{(gas)} + 2e^- \rightarrow \text{O}^{2-}, \quad \text{O}^{2-} + \text{V}_o^- \rightarrow \text{O}_0^= (6.1)$$

During the past decade, cathode performance at reduced temperatures has seen significant improvements, mainly by the use of mixed ionic electronic conductors (MIEC), which exhibit simultaneous oxygen ion and electron conduction. The introduction of ionic transport extends the active region for oxygen reduction from the electrolyte / electrode / gas phase triple phase boundary to the full electrode area [178], providing the superior overall electrode reaction rate.

Recently, several promising MIEC cathode materials, such as lanthanum strontium cobalt ferrite (LSCF), lanthanum strontium cobaltite (LSCo) and samarium strontium cobaltite (SSCo), were proposed for intermediate temperature range uses. These materials exhibit higher ionic and electronic conductivity and high catalytic activity for oxygen reduction than the conventional cathode material, lanthanum strontium manganite (LSM) [179-182].
The goal in developing SSEP catalysts was to develop a kind of non-precious metal catalyst with low operation temperature. Thus, adopting LSCF as the selective cathode of the SSEP catalyst should increase the performance of the SSEP catalysts. However, as shown in the catalytic performance of the new catalyst YLFNCCe, the performance is not as good as expected. After 30 min, the performance decreases significantly. The reason is that most of cobalt-containing cathode materials are known to react with a zirconia-based electrolyte even at around 800 °C to form highly resistive reaction products such as (Sr, Zr)O$_3$ [183-188]. Moreover, large differences in thermal expansion coefficients of these materials compared to that of YSZ causes attrition and thermal cycle stability.

6.4 Summary

Effect of replacing the major components with other materials with better functional properties is studied and discussed in this chapter. GDC, an alternative oxygen ionic conductor with a higher oxygen ion conductivity, is used to substitute the YSZ. The results indicate that this replacement with GDC as the oxygen ion conductor results in a better performance than that of YSZ based catalysts especially in the lower temperature range. Thus, increasing the oxygen ionic conductivity can increase the
performance of the SSEP catalysts. This further verifies the SSEP mechanism for the catalytic reforming process. LSCF is used to substitute LSM as the cathode. The results reveal that the performance of the SSEP catalyst based on the YSZ/LSCF is decreased, because of the reactions between YSZ and LSCF and formation of a non-catalytic material. Other materials, LSCF-GDC, YSZ-Sm$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$O$_{3}$ (SSCF), La$_{0.9}$Sr$_{0.1}$Gd$_{0.8}$Mg$_{0.2}$O$_{3}$ (LSGM)-LSCF are recommended to be used to replace LSM in order to yield a better performance. Generally speaking, higher specific surface area, high performance, as shown in the experimental results, all the specific surface area is almost 20 times lower than that of the commercial noble metal catalysts. Thus another possible way to increase the performance of the SSEP catalysts is increase the specific surface area by optimizing the composition and preparation of the SSEP catalysts [206, 212].
7.1 Literature review

7.1.1 Bonded structures in aviation industries

Reducing the weight of components is very important in aerospace engineering applications, since it yields significant fuel savings. Replacing mechanical fasteners with adhesive bonds is one effective way of reducing airplane weight. The main advantages adhesive bonding provides are: light-weight connections, their ability to join different materials with dissimilar thicknesses without galvanic corrosion, their ability to join heat-sensitive alloys, the fact that they can still produce bonds with unbroken smooth surfaces, their ability to bond small adherends, their near-uniform stress distributions, and their higher fatigue endurances. In aviation industries, cost savings of 60 - 70% are often realized in the assembly processes when adhesive bonding technology is utilized over mechanical means of permanent bonding [206].

Safety is the most crucial issue when it comes to commercial aviation. A significant bond-failure related accident was the Aloha flight 243 case in Hawaii, on April 28, 1988 [207], in which the bonded upper surface of the fuselage of a Boeing
737 separated in flight, leading to the death of one flight attendant. The aircraft landed with severe structural damage, and had failed due to the coalescence of a number of small cracks, the results of Multi-Site Damage. However, the reason the cracks formed was due to the failure of an adhesive bond at the fuselage splice joint. The problem was the use of room temperature air when curing film adhesive, which had to be frozen to prevent premature curing. Condensed water on the surface inhibited the formation of chemical intermolecular bonds, leading to de-bonding in-flight and subsequent cracking.

7.1.2 Technology of adhesive bonding

7.1.2.1 General

Adhesives [208] are defined as polymeric substances with visco-elastic behavior, capable of holding adherends together by surface attachment to produce a joint with high shear strength.

7.1.2.2 Adhesion by mechanical interlocking

If a substrate has an irregular surface, then the adhesive may enter the surface irregularities prior to hardening. This idea demystifies the mechanical interlocking theory [209], which applies to adhesive bonds between porous materials.
7.1.2.3 Adhesion by chemical intermolecular bonds

The chemical bonding theory of adhesion invokes the formation of covalent, ionic or hydrogen bonds or Lewis acid-base interactions across the interface [210].

7.1.2.4 Adhesives for aerospace application

There are two basic classes of adhesive bonding [210] in aerospace structures. The first class is structural bonds, with epoxy, phenolic, or acrylic adhesives, in which loads between members are transferred. The other class is sealants, to protect against corrosion at interfaces. Both classes of polymers stay in place for the life of the structure, although they have different stiffnesses.

7.1.3 Degradation of adhesive bonding

7.1.3.1 Fracture

The basic principle for the design of adhesive bonds is to design the joint such that the adhesive is always stronger than the unnotched strength of the adherends [213].
A design deficiency is characterized by fracture of the adhesive (cohesion failure). Processing deficiencies are usually characterized by interfacial failure (adhesion failure) (Figure 7.1) of the bond. The best adhesive only fail in cohesion failure mode.

![Cohesion Failure](image1) ![Adhesion Failure](image2)

Figure 7.1. Types of failure in adhesive bonds.

7.1.3.2 Fatigue

The fatigue [214] phenomenon is common to most types of materials and it has been estimated that 80% of all engineering failures can be attributed to fatigue.

7.1.3.3 Environmental effects and durability

All adhesives absorb water [210]. Concerns over absorbed moisture and its removal from composite materials during structural repair are well-established [215].

Adhesive layers in joints absorb water and vapor, and transmit it to the interface. This cannot be prevented by sealing the edges with a paint or lacquer, as these also
absorb water. Once within a joint, there are several possible ways by which water may cause weakening. These are reviewed by Comyn [216, 217].

7.1.4 Surface pretreatments

Surface pretreatment is the most important process governing the quality of an adhesive bond [218]. It increases the bond strength by altering the substrate surface in a number of ways including [219]: increasing surface tension, which increases the surface area and allows the adhesive to flow in and around the irregularities on the surface to form a mechanical bond, increasing surface roughness or providing interlock adhesion, and changing surface chemistry, which results in the formation of a chemical bond. For different adherends, the pretreatment method varies.

7.1.5 No certified technology available for in-field surface chemistry analysis

It is clear that all the existing methods have their limitations. None of them can provide in-field surface contamination detection for pre-bond surfaces. As a result, there is no method satisfying the requirement for online and in-field surface chemistry analyses specified by the FAA (Federal Aviation Administration). Because of lack of in-field surface chemistry analysis methods, the aviation industry
relies on complicated and tight procedure controls to ensure the quality of the pretreated surfaces. This involves a number of Standard Operation Procedures (SOPs) and certifications including composite material, adhesive, equipment, procedure, environment, and technician certifications. Without a definitive surface chemistry analysis method, the SOPs and certifications may result in excessive efforts and costs or insufficient quality of the pre-bond surface.

7.2 The operational principle for a solid-state electrochemical sensor

![Figure 7.2. Operation principle of solid-state ECS.](image)

The operation principle of the solid-state electrochemical sensor is schematically illustrated in Figure 7.2.
The left side of the schematic represents the surface of composite laminate being inspected. The silver electrode is used as the working electrode for current collecting. Between the surface and the silver electrode is a polymer electrolyte, in this case, a Nafion™ film is doped with a mediator. The mediators are compounds that can undergo fast electron transfer between the compound molecules, typically $\text{Ag}/\text{Ag}^+$, $\text{NaI}/\text{I}_2$ and $\text{K}_4\text{Fe(CN)}_6$. The composite surface may have dangling bonds with unsatisfied electronic orbitals or have contaminants that tend to be reduced or oxidized under certain electrochemical potentials. In this scenario, there is electron transfer between the composite surface and the mediators in the polymer electrolyte. The electrons, or “holes”, are further passed to the working electrode via electron transfer between the mediators in the polymer electrolyte and electron transfer between the mediators and the working electrode. These interactions result in a current that can be detected. Usually, substantial charge transfer occurs at one or several specific potentials at the interfaces. Therefore, at these potentials there is a current peak in a potential scan with a constant rate. Thus, both the potential value and current at these potentials are useful for evaluating the chemical state of the laminate surface. Two electrochemical measurement methods can be used to
evaluate the chemical state of the composite laminate surface: 1) cyclic voltammetry (CV) and 2) electrochemical impedance spectroscopy (EIS). The CV method requires lower internal and interface resistances than the electrochemical system.

The following experimental study is designated to demonstrate the feasibility of using the solid-state electrochemical sensor for in-field detection of contaminants and moisture on the composite surface.

7.3 Experimental

7.3.1 Preparation of the sensor

The fabrication of the electrochemical sensor for electrochemical impedance measurements in the field is desperately needed. The schematic of the proposed electrochemical sensor is shown in Figure 7.3. The working and counter electrodes are Ag strips painted on a Teflon sheet using a silver adhesive courtesy of Alfa Aesar. The reference electrode is also a strip painted on the Teflon sheet using the same silver adhesive blended with 30 wt% AgCl fine powder. The wet strips were first dried in a closed box overnight and then further fried in a vacuum oven overnight. The areas of the working and counter electrodes are 2 cm$^2$ and the gaps between the
working and reference electrodes and between the counter and reference electrode are 0.2 mm. The width of the reference electrode is 1.5 mm.

When the electrode strips were fully dried, they were covered with a thin Nafion™ film of 0.1-0.2 mm by dripping a Nafion™ 117 solution doped with NaI and I₂ (Alfa Aesar) on top of the Teflon sheet.

The film is dried naturally in the closed box environment. The Nafion™ solution is doped with NaI and I₂ via the following procedure. Measure out 20 mL of the Nafion™ solution containing 5 wt% of Nafion™ and volatile solvents. Also measure 0.02 mol of NaI and 0.01 mol of I₂. The solid chemicals were mixed with Nafion™ solution. The mixture was sonicated for 1 hour and kept in a closed vial.
7.3.2 Preparation of the coupon samples

7.3.2.1 Surface moisture control coupon samples

The acrylic coupon samples were prepared using the following procedure: 1.5 inch x 2.5 inch x 0.2 inch pieces were cut and the protective film was removed. The surface was washed with ethanol (99%) and then with deionized water. The coupon samples that were cleaned were then kept in a vacuum oven at 50 °C for 1 hour. This surface state was used as the baseline state. In the experiment, peel ply samples were also used. The samples were provided by Institute on Advanced Aircraft Composites at University of Washington. The baseline surface state for the peel ply samples is the fresh surface when the peel ply film was removed within 1 minute. These baseline surface states were not absolutely clean surfaces by any means, but it was much cleaner than the other surface states referred as “contaminated surfaces” in the present paper.
7.3.2.2 Coupon samples from Bombardier

The coupon samples used were plain weave carbon fiber specimens provided by Bombardier Aerospace. The geometry of the test coupon sample was shown in Figure 7.4.

![Figure 7.4. Test Sample Geometry.](image)

The details of contamination for the composite coupon samples are shown in Table 7.1. For each coupon sample, there are two areas.
The top one was cleaned using Diestone HFP cleanser whereas the bottom one was cleaned using MEK cleanser after a specific contamination process.

Table 7.1. Coupon Identification and Contaminants.

<table>
<thead>
<tr>
<th>Number</th>
<th>Coupon ID</th>
<th>Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FPR-1</td>
<td>Fingerprint Residue</td>
</tr>
<tr>
<td>2</td>
<td>UCG-1</td>
<td>Ultrasonic Coupling Gel</td>
</tr>
<tr>
<td>3</td>
<td>BC-1</td>
<td>Penetone Protective Cream 411</td>
</tr>
<tr>
<td>4</td>
<td>D-1</td>
<td>Dust</td>
</tr>
<tr>
<td>5</td>
<td>HFP-1</td>
<td>Cleanser (Diestone HFP)</td>
</tr>
<tr>
<td>6</td>
<td>MEK-1</td>
<td>Cleanser (MEK)</td>
</tr>
<tr>
<td>7</td>
<td>TR-1</td>
<td>Tape Residue no silicone (MTI RAE1000)</td>
</tr>
<tr>
<td>8</td>
<td>MRKR-1</td>
<td>Marker</td>
</tr>
<tr>
<td>9</td>
<td>BRCL-1</td>
<td>Breather Cloth</td>
</tr>
<tr>
<td>10</td>
<td>COLA-1</td>
<td>Soda</td>
</tr>
<tr>
<td>11</td>
<td>COF-1</td>
<td>Coffee</td>
</tr>
<tr>
<td>12</td>
<td>GR-1</td>
<td>Glove Residue</td>
</tr>
<tr>
<td>13</td>
<td>CTL-1</td>
<td>Control (UV dye in water only)</td>
</tr>
<tr>
<td>14</td>
<td>0-1 (Pristine)</td>
<td>None</td>
</tr>
</tbody>
</table>

7.3.3 Testing setup

The testing setup for the sensors is shown in Figure 7.5. The electrodes of the sensor were connected to a potentiostat controlled by a computer. The Nafion™ film of the sensor was placed on the top of a coupon sample to be tested. The electrodes were connected on the back of the sensor with a potentiostat (Gamry
Instruments). The sensor was slightly pressed to the coupon sample by placing a 1 kg weight on the top of the testing assembly.

![Experimental setup for electrochemical impedance spectroscopy method.](image)

**Figure 7.5.** Experimental setup for electrochemical impedance spectroscopy method.

### 7.3.4 Characterization

The common characterization methods for coupon samples include electrochemical characterization, SEM and EDS analyses.

#### 7.3.4.1 Electrochemical performance characterization

A GAMRY potentiostat/Galvanostat/ZRA analyzer was used to run all the electrochemical tests. Both electrochemical impedance spectroscopy (EIS) was taken at room temperature using solid-state electrochemical sensor.

Electrochemical Impedance Spectroscopy has been embraced by the corrosion
specialist and the battery, fuel cell and other electrochemical device researcher. The EIS data usually were used to build a nonlinear least-squares fitting routine model to extract physically meaningful properties of the electrochemical system and analyze the mechanism of its behavior. The EIS data may be get using Nyquist plot or Bode plot. The real and imaginary components of the impedance can also be plotted against frequency on a log-log scale; this type of plot is known as a Bode plot. To fit the EIS data in the frequency domain, model represents an equivalent circuit is required [230].

Because of the difference in the mechanisms of storing charges between the double-layer capacitor and the conventional capacitors, traditional capacitor models are inadequate for supercapacitors. A number of models currently exist that apply to the operation of double-layer capacitors.

The diagrams in Figure 7.6 represent a hierarchy of equivalent circuit, from those for a simple capacitor through those involving simple combinations of capacitor element with either one or two resistors or capacitor, to more complex equivalent circuits involving distributed capacitance with ohmic element in series or parallel coupling with capacitative element and resistances in parallel with the capacitative elements. Figure 7.6 (a) represents ideally polarizable interfacial capacitance by a
capacitance ($C_{dl}$). Figure 7.6 (b) represents interfacial capacitance in series with ohmic resistance.

![Figure 7.6](image)

Figure 7.6. Introduction to the hierarchy of equivalent circuits.

A simple model for a double-layer capacitor can be represented by a capacitance ($C_{dl}$) with an equivalent series resistance (ESR) and an equivalent parallel resistance (EPR) or pore resistance ($R_p$) as shown in Figure 7.6 (c). The ESR models power losses that may result from internal heating, which is of importance during charging and discharging. The EPR models current leakage, and influences long-term energy storage. By determining these three parameters, one is able to develop a first order approximation of electrical double-layer capacitor behavior. If EPR element changes into Faradaic leakage resistances, it indicates the contribution from
pseudocapacitance associated with surface redox functionalities. Figure 7.6 (d) is also called Randle circuit with a constant phase element (CPE) replacing the double layer capacity ($C_{dl}$). The difference to Figure 7.6 (c) is diffusion impedance –W–. While the simple model provides a first approximation of a double layer capacitor’s behavior, it is observed that there is a large error when compared with experimental results. In this way, more complicated equivalent circuit as shown in Figure 7.6 (e) and (f) is provided.

Figure 7.6 explains the hierarchy of equivalent circuit for (a) a simple capacitor (b) a capacitor with an equivalent series resistance (ESR) (c) a capacitor with an equivalent series resistance and an equivalent parallel resistance (EPR) (d) a capacitor with an equivalent series resistance and an equivalent parallel resistance (EPR) in series with a Warburg element (e) a parallel combination of n capacitors concluded by an EPR (f) parallel capacitors & EPR elements connected with pore-resistance elements, $R_p$ [231].

ESR reduction of supercapacitors is very important in order to compete with other storage devices. There are at least four different contributions to the ESR originating from the (i) electrolyte including separator, (ii) current collector, (iii)
porous layer including contact to current collector, and (iv) other contact resistances.

In order to prevent short circuits between neighboring capacitor electrodes, a porous separator has to be used as a spacer. Independent of the choice of electrolyte the spacer has to be thin and highly porous in order to keep the resulting resistance low.

7.3.4.2 Phys-chemical property characterization

SEM has been the most commonly used tool to characterize the morphology and topology of different samples. The surface morphologies of the composite electrolyte and electrode were investigated using scanning electron microscopy (JEOL JSM 5900LV) and Table-top SEM (Phenom). All the samples were covered gold film using a gold sputtering device before test. An Olympus BX60 light microscope with polarized light function is also used to observe the surface state of the membrane.

Since each element has a unique atomic structure, energy dispersive X-ray spectroscopy (EDAX or EDS) could be used for the elemental analysis through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. The energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic
structure of the element from which they were emitted. This allows the elemental composition of the specimen to be measured. EDAX systems are most commonly found on scanning electron microscopes (SEM-EDAX) and electron microprobes. A detector is used to convert X-ray energy into voltage signal and send to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis. According to P. Staiti [232], EDX analyses were performed on different regions, which are chosen from the SEM figure of each sample to determine representative values of potassium contents. Thus an atomic ratio calculated from EDAX is considered representative for all samples.

7.4 Results

7.4.1 Moisture and contaminant detection results

EIS tests were conducted on contaminated and non-contaminated coupon surfaces. Typical experiment results, Equivalent circuit and Simulation results are shown in Figure 7.7-Figure 7.12. Figure 7.7 and Figure 7.8 are the EIS and the simulation circuit results for a non-contaminated surface.
The real part of the impedance corresponding to the lowest imaginary part of the impedance is about $2.3 \times 10^5$ ohm. This value can be explained as the sum of the electrolyte resistance and charge transfer resistance.

![Impedance graph]

Figure 7.7. EIS of a non-contaminated acrylic plastic surface.

![Equivalent circuit diagram]

Figure 7.8. Equivalent circuit and values for EIS analysis or curve fitting.

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$</td>
<td>0 ohm</td>
</tr>
<tr>
<td>$R_1$</td>
<td>$1.5 \times 10^5$ ohm</td>
</tr>
<tr>
<td>$W_1-R$</td>
<td>$8.05 \times 10^4$ ohm</td>
</tr>
<tr>
<td>CPE1-T</td>
<td>$6 \times 10^{-9}$ F</td>
</tr>
</tbody>
</table>

Figure 7.9 and Figure 7.10 are the EIS and simulation results for the surface contaminated with tap water.
The surface was wiped with cleanroom wipes (Kimberly-Clark) for 3 times before being tested.

![Figure 7.9. EIS of an acrylic plastic surface contaminated with tap water](image)

Figure 7.9. EIS of an acrylic plastic surface contaminated with tap water.

![Figure 7.10. Equivalent circuit and value for EIS analysis or curve fitting](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>$2 \times 10^4$ ohm</td>
</tr>
<tr>
<td>R1</td>
<td>$1.5 \times 10^4$ ohm</td>
</tr>
<tr>
<td>W1-R</td>
<td>$1 \times 10^3$ ohm</td>
</tr>
<tr>
<td>CPE1-T</td>
<td>9.66 $\times 10^{-6}$ F</td>
</tr>
</tbody>
</table>

Figure 7.10. Equivalent circuit and value for EIS analysis or curve fitting.

Figure 7.11 and Figure 7.12 are the EIS and simulation results for the surface etched or contaminated with 50% H$_2$SO$_4$. The surface was washed with deionized water and then wiped with cleanroom wipes (Kimberly-Clark) for 3 times before being tested. The sum of the electrolyte resistance, Rs, and charge transfer
resistance, \( R_1 \), or impedance for the non-contaminated acrylic plastic surface is much greater than that of the contaminated surfaces.

![Graph showing EIS of an acrylic plastic surface contaminated with 50% H\(_2\)SO\(_4\).]

Figure 7.11. EIS of an acrylic plastic surface contaminated with 50% H\(_2\)SO\(_4\).

![Equivalent Circuit and value for EIS analysis or curve fitting.]

Figure 7.12. Equivalent Circuit and value for EIS analysis or curve fitting.

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s )</td>
<td>( 4.52 \times 10^3 ) ohm</td>
</tr>
<tr>
<td>( R_1 )</td>
<td>( 3 \times 10^3 ) ohm</td>
</tr>
<tr>
<td>W1-R</td>
<td>( 1 \times 10^3 ) ohm</td>
</tr>
<tr>
<td>CPE1-T</td>
<td>( 2.7 \times 10^{-6} ) F</td>
</tr>
</tbody>
</table>

More EIS measurement results are summarized in Figure 7.13 and Figure 7.14.

The ratios of impedance for contaminated and non-contaminated surfaces are listed in Table 7.2.
The ratios are in the range of 2.5 to 81.4. \( \text{H}_2\text{SO}_4 \) contaminated surfaces show greater ratios than tap water contaminated surfaces.

Table 7.2. Summary of the EIS results on contaminated and clean surfaces.

<table>
<thead>
<tr>
<th>Sensor number</th>
<th>Impedance for Contaminated surface ( \text{ohm} )</th>
<th>Impedance for non-contaminated surface ( \text{ohm} )</th>
<th>Ratio</th>
<th>Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 2.7 \times 10^4 )</td>
<td>( 7.0 \times 10^4 )</td>
<td>2.59</td>
<td>Tap water</td>
</tr>
<tr>
<td>2</td>
<td>( 3.7 \times 10^4 )</td>
<td>( 2.3 \times 10^5 )</td>
<td>6.22</td>
<td>Tap water</td>
</tr>
<tr>
<td>3</td>
<td>( 2.8 \times 10^4 )</td>
<td>( 1.0 \times 10^5 )</td>
<td>3.57</td>
<td>Tap water</td>
</tr>
<tr>
<td>1</td>
<td>( 2.96 \times 10^3 )</td>
<td>( 5.2 \times 10^4 )</td>
<td>17.6</td>
<td>Tap water</td>
</tr>
<tr>
<td>5</td>
<td>( 3.2 \times 10^3 )</td>
<td>( 7.0 \times 10^4 )</td>
<td>21.9</td>
<td>( \text{H}_2\text{SO}_4 )</td>
</tr>
<tr>
<td>6</td>
<td>( 7.0 \times 10^3 )</td>
<td>( 5.7 \times 10^5 )</td>
<td>81.4</td>
<td>( \text{H}_2\text{SO}_4 )</td>
</tr>
<tr>
<td>7</td>
<td>( 6.17 \times 10^3 )</td>
<td>( 7.6 \times 10^4 )</td>
<td>12.3</td>
<td>( \text{H}_2\text{SO}_4 )</td>
</tr>
</tbody>
</table>

Thus, the sum of the electrolyte resistance and charge transfer resistance or impedance can be used to qualify the surface contamination if a non-contaminated surface is properly chosen as a reference.
The correlation between number of times wiping with wet tissue and polarization impedance should be clear from Figure 7.13. As the surface is cleaned, it’s polarization impedance approaches that of a non-contaminated surface.

![Figure 7.13. Sum of the electrolyte resistance and charge transfer resistance or impedance vs. number of times of wiping with cleanroom paper tissue. The surface was contaminated with tap water.](image)

Similarly, using a dry tissue still gets the surface relatively clean, but at a much slower rate.
It can be argued from these graphs, that dry wiping does not get the surface as clean as a thorough wet-wiping does.

Figure 7.14. Sum of the electrolyte resistance and charge transfer resistance vs. number of times of wiping with cleanroom paper tissue. The surfaces were contaminated with 50% H$_2$SO$_4$.

### 7.4.2 Results of Bombardier coupon samples

In order to find the correlation between the composition of the contamination and the electrochemical impedance spectroscopy (EIS) measurement results using the electrochemical sensor, EIS measurements were conducted on part of the coupon samples whereas scanning electron microscopy (SEM) and energy dispersive of X-ray spectroscopy (EDS) analyses were conducted the other part of
the coupon samples to image contaminants and evaluate the composition of contaminants.

7.4.2.1 Pristine sample

Figure 7.15. SEM of the pristine sample surface.

Figure 7.15 is the SEM result for the pristine samples and the surface is very clean and without contaminations.
From the area and point EDS results shown in Table 7.3 and Table 7.4, we can find the pristine sample mainly contains the elements C, O, F, Al and Br.

Table 7.3. Element weight percentages for the pristine sample surface area EDS.

<table>
<thead>
<tr>
<th>Element Line</th>
<th>Net Counts</th>
<th>K-Ratio</th>
<th>Weight %</th>
<th>Weight % Error</th>
<th>Atom %</th>
<th>Atom % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>260</td>
<td>0.71</td>
<td>67.02</td>
<td>+/- 3.61</td>
<td>78.75</td>
<td>+/- 4.24</td>
</tr>
<tr>
<td>O K</td>
<td>63</td>
<td>0.07</td>
<td>18.45</td>
<td>+/- 3.22</td>
<td>16.27</td>
<td>+/- 2.84</td>
</tr>
<tr>
<td>F K</td>
<td>16</td>
<td>0.02</td>
<td>4.25</td>
<td>+/- 2.39</td>
<td>3.15</td>
<td>+/- 1.77</td>
</tr>
<tr>
<td>Br K</td>
<td>18</td>
<td>0.00</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Br L</td>
<td>158</td>
<td>0.21</td>
<td>10.29</td>
<td>+/- 1.89</td>
<td>1.82</td>
<td>+/- 0.33</td>
</tr>
<tr>
<td>Br M</td>
<td>0</td>
<td>0.00</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>100.00</td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.4. Elemental weight percentages for pristine sample surface point EDS.

<table>
<thead>
<tr>
<th>MRKR(13)_pt1</th>
<th>C-K</th>
<th>O-K</th>
<th>F-K</th>
<th>Al-K</th>
<th>Au-L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>54.35</td>
<td>13.63</td>
<td>0.56</td>
<td>3.89</td>
<td>27.58</td>
</tr>
</tbody>
</table>

The element Au comes from the gold coating that is required in the steps to prepare a sample for SEM analyses.
7.4.2.2 Dust

As shown in Figure 7.16, there are some contaminants on the surface. The EDS results shown in Notice from the information in Table 7.5 that what is nebulously called “dust” is actually a collection of many tiny impurities.

Table 7.5 indicate that the contaminants mainly contain C, O, F, Mg, Al, Si, Cl, S, K, Ca, Ti, Cr, Fe, Zn and Br.
Notice from the information in Table 7.5 that what is nebulously called “dust” is actually a collection of many tiny impurities.

Table 7.5. Elemental weight percentages for area-analyzed EDS of dust.

<table>
<thead>
<tr>
<th>Element Line</th>
<th>Net Counts</th>
<th>K-Ratio</th>
<th>Weight %</th>
<th>Weight % Error</th>
<th>Atom %</th>
<th>Atom % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>4909</td>
<td>0.69</td>
<td>68.24</td>
<td>+/- 1.28</td>
<td>80.06</td>
<td>+/- 1.50</td>
</tr>
<tr>
<td>O K</td>
<td>930</td>
<td>0.05</td>
<td>17.27</td>
<td>+/- 1.49</td>
<td>15.21</td>
<td>+/- 1.31</td>
</tr>
<tr>
<td>F K</td>
<td>115</td>
<td>0.01</td>
<td>1.81</td>
<td>+/- 0.62</td>
<td>1.35</td>
<td>+/- 0.46</td>
</tr>
<tr>
<td>Al K</td>
<td>1715</td>
<td>0.05</td>
<td>3.12</td>
<td>+/- 0.14</td>
<td>1.63</td>
<td>+/- 0.07</td>
</tr>
<tr>
<td>Si K</td>
<td>364</td>
<td>0.01</td>
<td>0.64</td>
<td>+/- 0.07</td>
<td>0.32</td>
<td>+/- 0.04</td>
</tr>
<tr>
<td>Si L</td>
<td>0</td>
<td>0.00</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Ca K</td>
<td>147</td>
<td>0.01</td>
<td>0.39</td>
<td>+/- 0.08</td>
<td>0.14</td>
<td>+/- 0.03</td>
</tr>
<tr>
<td>Ca L</td>
<td>0</td>
<td>0.00</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Nb K</td>
<td>6</td>
<td>0.00</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Nb L</td>
<td>3503</td>
<td>0.18</td>
<td>8.52</td>
<td>+/- 0.43</td>
<td>1.29</td>
<td>+/- 0.07</td>
</tr>
<tr>
<td>Nb M</td>
<td>297</td>
<td>0.00</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>100.00</td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the same way that EDS was used to characterize elements in the SSEP catalysts, this tool was used again for the same purpose, just with dust instead of catalysts.
As can be seen from Figure 7.17, the EDS on this sample shows the entire set of elements found on the sample.

![EDS Chart](image)

Figure 7.17. EDS of the sample Dust surface.

The EDS analysis and EIS measurement results were summarized in Table 7.6. These data reveal that the pristine surface has the highest polarization impedance whereas the contaminated coupon samples that contain other elements found on the pristine samples have lower polarization impedances.
It goes to show that polarization impedance is an accurate way of measuring the surface oxidation state and identifying surface contaminants.

Table 7.6. Summary of composition of the contaminants on surfaces of the coupon samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[O] wt%</th>
<th>[Al] wt%</th>
<th>[K] wt%</th>
<th>[Si] wt%</th>
<th>[Na] wt%</th>
<th>[S] wt%</th>
<th>[Fe] wt%</th>
<th>[Zn] wt%</th>
<th>Polarization Impedance (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>13.63</td>
<td>3.89</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.0 \times 10^6$</td>
</tr>
<tr>
<td>Cleanser HFP</td>
<td>15.89</td>
<td>6.47</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.53</td>
<td>$1.8 \times 10^5$</td>
</tr>
<tr>
<td>UV dye</td>
<td>13.70</td>
<td>0.60</td>
<td>0.28</td>
<td>0</td>
<td>1.33</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$6.0 \times 10^5$</td>
</tr>
<tr>
<td>Ultrasonic Coupling gel</td>
<td>36.45</td>
<td>5.67</td>
<td>8.03</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$6.0 \times 10^5$</td>
</tr>
<tr>
<td>Silicone rubber glove residue</td>
<td>9.05</td>
<td>8.28</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>22.89</td>
<td>0</td>
<td>0</td>
<td>$1.8 \times 10^6$</td>
</tr>
<tr>
<td>Solution from a marker</td>
<td>18.43</td>
<td>2.56</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$8.0 \times 10^5$</td>
</tr>
<tr>
<td>Tape Residue</td>
<td>11.28</td>
<td>3.04</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$1.7 \times 10^6$</td>
</tr>
<tr>
<td>Soda</td>
<td>26.57</td>
<td>0.57</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12.1</td>
<td>0</td>
<td>$6.5 \times 10^5$</td>
</tr>
<tr>
<td>Coffee</td>
<td>15.73</td>
<td>0.93</td>
<td>2.07</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$6.0 \times 10^5$</td>
</tr>
<tr>
<td>Protective Cream</td>
<td>6.39</td>
<td>0.13</td>
<td>0.82</td>
<td>0</td>
<td>1.31</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$1.2 \times 10^3$</td>
</tr>
<tr>
<td>Dust</td>
<td>18.54</td>
<td>5.80</td>
<td>3.47</td>
<td>2.07</td>
<td>1.64</td>
<td>2.47</td>
<td>8.90</td>
<td>0</td>
<td>$2.0 \times 10^4$</td>
</tr>
<tr>
<td>Fingerprint Residue</td>
<td>13.1</td>
<td>3.25</td>
<td>0</td>
<td>0</td>
<td>5.56</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.5 \times 10^4$</td>
</tr>
<tr>
<td>Cleanser MEK</td>
<td>31.50</td>
<td>3.80</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$4.9 \times 10^4$</td>
</tr>
</tbody>
</table>
7.5 Discussion

It is very clear by viewing Figure 7.14 and Figure 4.15 that the impedance correlates with the times of wiping with cleanroom tissue after contaminating the sample surface with sulfuric acid. In the case of contamination with tap water, the impedance approaches to the value for the pristine sample surface. This tendency is similar to that for the surface contaminated with sulfuric acid. However, the impedance seems to require more numbers of times of wiping to approach the value for the pristine sample surface. This indicates that the contamination by sulfuric acid is more difficult to be removed with cleanroom wipes that the contamination by tap water. It is also worth noticing that the results of the EIS measurements are different for non-contaminated surfaces. Whether this is due to the variations of the surface chemistry or the properties of the sensors is unknown. A confirmation of the reason requires an analysis using standard methods including X-ray photoelectron spectroscopy. In any case, detection of surface contamination requires use of a “reference” surface or a surface that is considered as clean. The impedance value
obtained with a sensor on a contaminated surface has to be compared with that obtained from the “reference” surface. The contamination level can be scaled with ratio of the impedance.

Sulfuric acid is considered as a very severe contamination. The sensitivity of the sensor has to be tested with less severe contaminations such as those made by Bombardier on commercial peel ply composite materials. The surfaces of the composite were contaminated with various substances including Diestone HFP cleanser, UV dye, ultrasonic coupling gel, silicone glove residue, solution from marker, tape residue (no silicone, MTI RAE1000), soda, coffee and protective cream. The impedance for the protective cream had the smallest value ($1.2 \times 10^3$ ohm) while the uncontaminated surface had the largest ($2 \times 10^6$ ohm). Results correlated well with the EDAX measurements from these laminate surfaces. This study demonstrated that the electrochemical sensors are effective in discriminating “clean” or “pristine” laminate surfaces and surfaces contaminated with a range of substances.

Human skin was found to be one of that the major sources of the dust [233]. According to R. Hollands’ study, the human skin mainly contains P, S, Cl, K, Ca, Fe,
and Cd [234]. Figure 7.16 shows that the contaminants on the surface of the Dust sample. The EDS of a contaminant is shown in the Figure 7.17. This contaminant mainly contains C, O, F, Mg, Al, Si, Cl, S, K, Ca, Ti, Cr, Fe, Zn and Br, including those major elements in the skin, S, Cl, K, Ca, and Fe. Thus, we can conclude that the contaminant found on the Dust sample surface may be a combination of skin and other substances. Usually, the body or hand cream or other protective cream contain the following elements, Ca, S, Fe, Hg, Mg, Mn, Ti, Ni and Zn [235-237]. The EDS result of the protective cream sample surface indicate that the contaminant mainly contain N, Cl, Na, Ca, Ti, Zn, Si, Fe, K, and Nb, including those major elements in the cosmetic, Ca, Zn, Ti and Fe.

From Table 7.6, there is correlation between the EIS impedance and surface contamination. The pristine laminate sample has the highest impedance among those of other samples. This is due to that the contaminants can react with mediators in the working electrode of the sensor, resulting in a higher AC current at a specific applied AC potential. Thus, the impedance which is the ratio of the AC potential to AC current is lower when there are contaminants.
7.7 Summary

All solid-state electrochemical sensors were prepared. The electrochemical tests based on the EIS were conducted on coupon samples made from an acrylic plastic material or from a commercial peel ply composite material provided by Bombardier Aerospace. The experiments results demonstrate that the feasibility of the solid state electrochemical sensor. The new solid state electrochemical sensor is sensitive and reliable for the surface quality control. It can be used to evaluate the moisture and contamination levels. Although different types of contaminations including soda, coffee, and dust fingerprint residue and so on, give different impedance values, identification of the types of contaminations requires more detailed surface chemistry analyses including XPS.
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