Present to National Energy Technology Laboratory
U. S. Department of Energy

Final Report
of
DOE Project (DE-AC26-99FT40709)

Lower Temperature Electrolyte and Electrode Materials

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April 30, 2003

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A Siemens Company

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ABSTRACT

A thorough literature survey on low-temperature electrolyte and electrode materials for SOFC is given in this report. Thermodynamic stability of selected electrolyte and its chemical compatibility with cathode substrate were evaluated. Preliminary electrochemical characterizations were conducted on symmetrical cells consisting of the selected electrolyte and various electrode materials. Feasibility of plasma spraying new electrolyte material thin-film on cathode substrate was explored.
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EXECUTIVE SUMMARY

A thorough literature survey on low-temperature electrolyte and electrode materials was conducted in an effort to identify the state-of-art materials. The survey strongly suggests the Sr- and Mg-doped LaGaO$_3$ (LSGM) as the electrolyte candidate and mixed electronic and oxide-ion conductors as the electrode candidates for low-temperature SOFCs. The advantages of using perovskite electrolyte LSGM are the high oxide-ion conductivity at lower temperature and excellent structural and chemical compatibility with perovskite cathode substrates. Selection of mixed conducting electrode is aimed at improving the electrode kinetics at lower temperatures. A composite mixed conducting electrode is considered technically viable.

The thermodynamic stability of LSGM electrolyte in CO$_2$-containing atmospheres was assessed by both theoretical analysis and experimental studies. Theoretical calculation predicted that lower temperature and high CO$_2$ condition is favorable for carbonates formation. Subsequent experiments using molten salt technique with adequate salt system such as KCl-NaCl and Na$_2$CO$_3$-K$_2$CO$_3$ proved that LSGM is stable in CO$_2$ atmosphere to the detection limit of X-ray diffraction. Supportive evidences were also provided by TGA measurement, see Figure A, where only a negligible weight-gain in CO$_2$-containing atmospheres at 800°C was found in dense LSGM ceramic samples. In addition, the carbonate process was found reversible upon CO$_2$ concentration.

![Figure A TGA curve of LSGM ceramics at 800°C in various CO$_2$-containing atmospheres](image)

The chemical compatibility of LSGM films with SWPC cathode substrate was evaluated using EBMA technique. The LSGM layer deposited by slurry dip-coating technique was gas-tight by sintering at above 1450°C. A typical microstructure was shown in Figure B. However, the chemistry of the LSGM film was found greatly altered due to extensive chemical interdiffusion found primarily between Mn and Ga at elevated temperatures, which promoted the formation of insulating phases in LSGM. The results clearly
suggested a lower densification temperature be required in order to alleviate the observed chemical diffusion.

Figure B LSGM thin-film on SWPC cathode substrate after firing at 1475°C for 3 hours

Preliminary electrochemical characterizations on LSGM-based symmetrical cells were performed using AC impedance and DC polarization techniques. Various cathode materials were tested from 600 to 800°C in air, among which Sr- and Fe-doped LaCoO₃ perovskite showed the lowest polarization for oxygen reduction.

Feasibility of making LSGM thin-film on SWPC cathode substrate was explored with plasma spray technique. The results evidently demonstrated that a successful deposition of LSGM film is achievable with right initial chemical composition of LSGM powder feedstock and adequate plasma spray parameters. Figure C showed a typical cross-sectional microstructure of LSGM film on a SWPC substrate and a physical look of the coating. Due to the fact that the plasma sprayed LSGM films have the tendency of being amorphous, a temperature greater than 800°C was found to be necessary for the crystallization. Under such a low temperature, no significant chemical reaction is expected to occur between LSGM and cathode substrate.

Figure C Plasma sprayed LSGM thin-film on SWPC cathode substrate
1 LITERATURE SURVEY ON LOW TEMPERATURE ELECTRODE AND ELECTROLYTE MATERIALS

1.1 Introduction

Development of low-temperature solid oxide fuel cells (SOFCs) has been one of the ultimate goals pursued by the US Department of Energy for many years. The significance of this development is the potential cost reduction in both material and BOP, which has been the principal challenges during the course of SOFC commercialization. In principle, the new low-temperature electrodes are anticipated to maintain the catalytic activity of high-temperature ones for both oxygen reduction and fuel oxidation process, and the new low-temperature electrolyte is expected to be as conductive as those of high-temperature ones. The former requirement necessitates a development of new electrode materials or at least an optimization of existing materials in order to maximize the three-phase boundary length. The latter requires a discovery of new electrolyte system with higher oxide-ion conductivity at lower temperature. These developments are believed to be crucial towards developing lower-temperature SOFCs.

In this literature survey, we review recent and past developments in the field of solid electrolytes and mixed-conducting electrodes. The oxide-ion conductivity, chemical stability and structural compatibility of low-temperature electrolyte and electrode materials are particularly reviewed.

1.2 Solid Oxide Electrolytes

Good solid oxide electrolytes are generally found in two crystallographic families, namely face-centered fluorite and primitive cubic perovskite structures. In the following, the review is organized according to this categorization.

1.2.1 Oxide electrolytes with fluorite structure

Fluorite oxides are historically the most studied materials for use as oxide-ion conductors in electrochemical devices, mainly due to the structural favoring for oxide-ion migration and ease of creating oxygen vacancies. A representative of fluorite solid electrolytes is the stabilized ZrO$_2$. Pure ZrO$_2$ is known to exhibit progressively three types of crystallographic polymorphs- monoclinic, tetragonal and cubic, respectively, as the temperature increases. Despite pure ZrO$_2$ is neither an electronic nor an oxide-ion conductor, its oxide-ion conductivity can be considerably enhanced by suitably doping a lower-valence cation in the place of Zr. The common dopants include alkaline- and rare-earth ions such as Sr$^{2+}$, Ca$^{2+}$, Sc$^{3+}$ and Y$^{3+}$. The doping leads not only to an increase in oxide-ion conductivity as a result of increased numbers of oxygen vacancies, but also stabilizing the cubic phase from high-temperature to room temperature. Among various dopants, the radius of a dopant is believed to play an important role on oxide-ion conductivity. It is found that the closer the dopant radius to that of Zr$^{4+}$ ($r$(VIII)= 0.84 Å) is, the higher the conductivity will be. Immediate examples are Zr$_{0.9}$Sc$_{0.1}$O$_{1.95}$ (ScSZ) ($r$(Sc$^{3+}$, VIII)= 0.87 Å) that has a conductivity of 0.1 S/cm at 800°C whereas Zr$_{0.9}$Y$_{0.1}$O$_{1.95}$ (herein after referred to YSZ) ($r$(Y$^{3+}$, VIII)= 1.02 Å) has a conductivity of 0.03 S/cm at the same temperature.
To lower the operating temperature of a SOFC requires an improvement in oxide-ion conductivity of electrolyte. From a crystallographic point of view, oxide-ions in the fluorite structure must pass a bottleneck consisting of three cations located at the vertexes of one of the triangular faces of its coordination tetrahedron in order to migrate from one tetragonal site to another. One of easiest ways to make such a passage is to make the cations more polarizable. As the polarizability of an ion increases with its ionic size, larger cations are expected to give higher oxide-ion conductivity. To maintain the stability of the fluorite structure, however, the cation/anion radius ratio must be kept close to 0.70. Considering oxide-ion radius of 1.38 Å, the optimal cation size appears to be 1 Å. Such large 4+ cations can only be found among 4f, 5f and 6p elements. Immediate examples are cerium, uranium and bismuth oxides.

Ceria-based solid solutions have been extensively studied as possible substitutes of ZrO$_2$-based electrolytes potentially used in SOFCs for the past several decades. As discussed above, its conductivity is generally higher than that of ZrO$_2$-based solid electrolytes. For instance, Gd-doped CeO$_2$ has an oxide-ion conductivity of five times higher than that of YSZ in air as shown in Figure 1-1. Among CeO$_2$-based electrolytes, Sm-doped CeO$_2$ exhibits the highest oxide-ion conductivity$^1$. Despite of the fact that electrical conductivity of CeO$_2$-family shows promise to replace the YSZ, the potential of being reduced under a reducing atmosphere, which is due to the mixed valence of Ce$^{4+}$/Ce$^{3+}$ redox couple, limits considerably its applications in SOFCs. The reduction of Ce$^{4+}$ has double adversary impacts: introduction of the unwanted electronic conduction, leading to a loss of cell efficiency, and dramatic dimensional changes as a result of lattice oxygen loss, leading to a warping or cracking of CeO$_2$ membranes. A proposed solution to circumvent this problem is to coat a thin protective layer of YSZ on the fuel electrode side$^2$,$^3$, but a reaction between ZrO$_2$ and CeO$_2$ has been found during fabrication and long-term operation, which increases the cell ohmic resistance$^4$.

It is no doubt that a high oxide-ion conductivity is an essential requirement for a solid electrolyte. The chemical stability in both oxidizing and reducing atmospheres as well as chemical compatibility with electrodes are equally important for SOFC applications. ZrO$_2$-based solid electrolytes are known to have excellent chemical stability in either oxidizing or reducing atmosphere, but the chemical reactivity with La in the cathode at elevated temperatures needs to be carefully addressed during the course of manufacturing SOFCs. This issue will be further discussed in the following section.

1.2.2 Oxide electrolytes with perovskite structure

One class of materials that also exhibits high oxide-ion conductivity is based upon the perovskite structure. Oxides with perovskite structure, which have the generic formula ABO$_3$, are one of the most versatile classes of solid oxides known. They can structurally accommodate a wide range of cations and exhibit a variety of conductivity behaviors, ranging from predominantly electronic (e. g. LaNiO$_3$)$^5$ to almost purely ionic (e. g. doped LaGaO$_3$)$^6$,$^7$. Extrinsic oxygen vacancies can be easily created in the perovskite by doping lower-valence cations at both A and/or B sites or, alternatively, the vacancies can be intrinsic to the structure, as in the case of the highly oxygen-deficient brownmillerite. A comparison of conductivities in perovskite and fluorite electrolytes is given in Figure 1-
where oxide-ion conductivities ranging from essentially zero to equaling or exceeding that of stabilized zirconia are clearly seen.

Figure 1-1 Arrhenius plots of oxide-ion conductivity of ceria-based oxides doped with rare-earth oxides. O—(CeO$_2$)$_{0.8}$(SmO$_{1.5}$)$_{0.2}$; △—(CeO$_2$)$_{0.8}$(GdO$_{1.5}$)$_{0.2}$; V—(CeO$_2$)$_{0.8}$(YO$_{1.5}$)$_{0.2}$; □—(CeO$_2$)$_{0.8}$(CaO)$_{0.2}$; ■—CeO$_2$; ●—(ZrO$_2$)$_{0.8}$(YO$_{1.5}$)$_{0.15}$.
In 1990, Goodenough et al. \(^9\) first pointed out the possibility of high oxide-ion conductivity existing in perovskites or perovskite-related intergrowth by demonstrating an oxygen vacancy order-disorder transition at 930°C in the brownmillerite \(\text{Ba}_2\text{In}_2\text{O}_5\). The activation energy for disordered oxygen vacancies is very close to that observed in the fluorite structure. Since then, a number of doped perovskites have been reported to exhibit appreciable oxide-ion conductivity. Among these perovskite oxides, doped \(\text{LaGaO}_3\) is the leading solid oxide electrolyte discovered recently. Table 1-1 lists the oxide-ion conductivities at 700°C for a number of oxygen-deficient perovskites.

**Table 1-1 Oxide-ion conductivity for selected perovskite oxides**

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<th>T(°C)</th>
<th>(\sigma) (S/cm)</th>
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<tr>
<td>(\text{NdAlO}_3)</td>
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<td>(1x10^{-5})</td>
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<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{AlO}_3)</td>
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<td>(8x10^{-4})</td>
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<tr>
<td>(\text{Nd}<em>{0.9}\text{Ba}</em>{0.1}\text{AlO}_3)</td>
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<td>6</td>
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<tr>
<td>(\text{Nd}<em>{0.9}\text{Ca}</em>{0.1}\text{AlO}_3)</td>
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<td>11</td>
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<tr>
<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.5}\text{Ga}</em>{0.5}\text{O}_3)</td>
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<td>(5x10^{-3})</td>
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<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.9}\text{Co}</em>{0.1}\text{O}_3)</td>
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<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.9}\text{Cu}</em>{0.1}\text{O}_3)</td>
<td>700</td>
<td>(5x10^{-3})</td>
<td>7</td>
</tr>
<tr>
<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.9}\text{Ni}</em>{0.1}\text{O}_3)</td>
<td>700</td>
<td>(1x10^{-3})</td>
<td>7</td>
</tr>
<tr>
<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.9}\text{Be}</em>{0.1}\text{O}_3)</td>
<td>700</td>
<td>(1x10^{-3})</td>
<td>7</td>
</tr>
<tr>
<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.9}\text{Zr}</em>{0.1}\text{O}_3)</td>
<td>700</td>
<td>(5x10^{-4})</td>
<td>7</td>
</tr>
<tr>
<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.9}\text{Mg}</em>{0.1}\text{O}_3)</td>
<td>700</td>
<td>(5x10^{-4})</td>
<td>7</td>
</tr>
<tr>
<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.9}\text{Si}</em>{0.1}\text{O}_3)</td>
<td>700</td>
<td>(1x10^{-4})</td>
<td>7</td>
</tr>
<tr>
<td>(\text{Nd}<em>{0.9}\text{Sr}</em>{0.1}\text{Al}<em>{0.9}\text{Zn}</em>{0.1}\text{O}_3)</td>
<td>700</td>
<td>(3x10^{-4})</td>
<td>7</td>
</tr>
<tr>
<td>(\text{CaCe}<em>{0.5}\text{Er}</em>{0.5}\text{O}_3)</td>
<td>700</td>
<td>(7x10^{-3})</td>
<td>12</td>
</tr>
<tr>
<td>(\text{BaTi}<em>{0.9}\text{In}</em>{0.1}\text{O}_3)</td>
<td>700</td>
<td>(5x10^{-2})</td>
<td>8</td>
</tr>
<tr>
<td>(\text{SrZrO}_3)</td>
<td>750</td>
<td>(4.3x10^{-3})</td>
<td>13</td>
</tr>
<tr>
<td>(\text{La}<em>{0.9}\text{Sr}</em>{0.1}\text{Ga}<em>{0.2}\text{O}</em>{2.95})</td>
<td>700</td>
<td>(1x10^{-2})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{La}<em>{0.9}\text{Ca}</em>{0.1}\text{Ga}<em>{0.2}\text{O}</em>{2.95})</td>
<td>700</td>
<td>(3x10^{-3})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{La}<em>{0.9}\text{Ba}</em>{0.1}\text{Ga}<em>{0.2}\text{O}</em>{2.95})</td>
<td>700</td>
<td>(3x10^{-3})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{La}<em>{0.9}\text{Sr}</em>{0.1}\text{Ga}<em>{0.9}\text{Al}</em>{0.1}\text{O}_{2.95})</td>
<td>700</td>
<td>(5x10^{-2})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{La}<em>{0.9}\text{Sr}</em>{0.1}\text{Ga}<em>{0.9}\text{Al}</em>{0.1}\text{O}_{2.95})</td>
<td>700</td>
<td>(2x10^{-2})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{La}<em>{0.9}\text{Sr}</em>{0.1}\text{Ga}<em>{0.9}\text{Mg}</em>{0.1}\text{O}_{2.90})</td>
<td>700</td>
<td>(6x10^{-2})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{La}<em>{0.9}\text{Sr}</em>{0.1}\text{Ga}<em>{0.9}\text{Mg}</em>{0.1}\text{O}_{2.85})</td>
<td>700</td>
<td>(7x10^{-2})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{Ga}<em>{0.83}\text{Mg}</em>{0.17}\text{O}_{2.815})</td>
<td>700</td>
<td>(9x10^{-2})</td>
<td>14</td>
</tr>
<tr>
<td>(\text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{Ga}<em>{0.83}\text{Mg}</em>{0.17}\text{O}_{2.815})</td>
<td>800</td>
<td>(1.8x10^{-1})</td>
<td>10</td>
</tr>
</tbody>
</table>

In 1994, the Sr- and Mg-doped \(\text{LaGaO}_3\), hereinafter denoted as LSGM, was first reported in both Ishihara’s (Japan) and Goodenough’s groups (The University of Texas at Austin) \(^2,3\). The AC conductivity of the LSGM was reported to be 0.10 S/cm at 800°C for the composition of \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\), and further improved to 0.17 S/cm at the same temperature for the composition of \(\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}\) as a result of increased numbers of oxygen vacancies and purer phase \(^10\). Soon after its discovery as an oxide-ion conductor, single SOFCs based on the LSGM were demonstrated to have very encouraging high power density even with a thick film (>500 μm) \(^15\). Table 1-2
summarized the progress from year 1995 to 2000 on thick-film LSGM-based SOFC achieved in The University of Texas at Austin. It is evident from Table 1-2 that the LSGM electrolyte is a strong candidate for low-temperature SOFCs.

<table>
<thead>
<tr>
<th>Years</th>
<th>LSGM electrolyte</th>
<th>Air-electrode/fuel-electrode</th>
<th>$V_{cell}(V)_{@800°C}$</th>
<th>MPD@$800°C$ (mW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995-97</td>
<td>$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$</td>
<td>LSCo40/SDC20+NiO</td>
<td>0.75</td>
<td>270</td>
</tr>
<tr>
<td></td>
<td>L= 500 µm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1998</td>
<td>$La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$</td>
<td>LSCo40/SDC20+NiO</td>
<td>0.85</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td>L= 500 µm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1999</td>
<td>$La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$</td>
<td>LSCo40/SDC20/SDC20+NiO</td>
<td>0.90</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>L= 550 µm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>$La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$</td>
<td>SCF/SDC20+NiO</td>
<td>0.97</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>L= 600 µm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: LSCo40=$La_{0.6}Sr_{0.4}CoO_{3-δ}$; SDC20= Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$; SCF= SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$; LDC40= Ce$_{0.6}$La$_{0.4}$O$_{1.8}$

Although perovskite electrolytes show superior conductivity performance, concerns on their chemical stability may arise when they are practically exposed to CO$_2$ and H$_2$O atmospheres. It is generally true that the larger A-cation that coordinates 12 oxygen atoms determines the chemical stability in oxygen containing atmospheres such as CO$_2$ and H$_2$O, while the smaller B-cation determines the chemical stability in reducing atmospheres. This is because a larger A-cation has a greater tendency to attract additional oxygen in CO$_2$ and H$_2$O in the presence of large amount of oxygen vacancies to fulfill the coordination requirement. Therefore, most of A (Sr and Ba) perovskites have very poor chemical stability in CO$_2$ and H$_2$O atmospheres. On the other hand, main group elements as B-cations with fixed valence are strongly preferred for solid electrolyte application since any mixed valence would induce unwanted electronic conduction.

As a summary of this section, some important properties of LSGM and YSZ, which appear to be a pair of competitors for electrolytes used in low-temperature SOFC, are compared in Table 1-3. In addition to much improved oxide-ion conductivity than that of YSZ, LSGM has excellent chemical and structural compatibility with most of the perovskite cathode materials, particularly mixed conductors. This advantage offers a possibility of co-sintering LSGM with cathode materials.

1.3 Cathode Materials

Doped LaMnO$_3$ perovskites are the most successful cathode materials to date for ZrO$_2$-based SOFCs. This material was adopted by the industry primarily based on the considerations on catalytic activity for oxygen reduction, chemical stability and thermal expansion match to the YSZ electrolyte. For example, the Siemens Westinghouse tubular SOFC’s cathode has been proven to possess reasonably good catalytic activity
at high temperatures (~1000°C) and a good thermal expansion match to the electrolyte (TEC = 10.5 × 10^{-6} /K vs 10.9 × 10^{-6} /K).

<table>
<thead>
<tr>
<th></th>
<th>LSGM</th>
<th>YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Primitive cubic</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>AC Conductivity</td>
<td>0.17 S/cm @ 800°C</td>
<td>0.12 S/cm @ 1000°C</td>
</tr>
<tr>
<td>Ionic transport number</td>
<td>( t_{\text{ion}} = 1.0 )</td>
<td>( t_{\text{ion}} = 1.0 )</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hardness (GPa) = 7.8±0.4</td>
<td>Hardness (GPa) = 12</td>
</tr>
<tr>
<td></td>
<td>Elastic modulus (GPa) = 187</td>
<td>Elastic modulus (GPa) = 200</td>
</tr>
<tr>
<td></td>
<td>Poisson’s ratio = 0.29</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fracture Toughness (MPa·m^{1/2}) = 1.11±0.10</td>
<td>Fracture Toughness (MPa·m^{1/2}) = 11</td>
</tr>
<tr>
<td>Chemical stability in CO₂-containing atmosphere</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Chemical compatibility at air-electrode interface</td>
<td>Excellent, no chemical reactions occurred</td>
<td>Poor, the La₂Zr₂O₇ phase commonly formed</td>
</tr>
<tr>
<td>Chemical compatibility at fuel-electrode interface</td>
<td>Poor, La-diffusion occurred</td>
<td>Excellent, no chemical reaction occurred</td>
</tr>
</tbody>
</table>

However, an appreciable performance reduction at lower-temperature range (T<950°C) is frequently observed, mainly due to electrode polarization for a thin-film electrolyte. For instance, the electrolyte area specific resistance (ASR) is 0.20 Ω·cm² at 800°C for a 40 µm-thick YSZ assuming a conductivity of 0.02 S/cm while the overall cell ASR is greater than 1.0 Ω·cm² at the same temperature. To maintain catalytic activity of cathode at low temperatures is one of key issues needed to be addressed for developing low-temperature SOFCs. Doped LaMnO₃ is known to be a solely electronic conductor. The oxygen reduction can only take place at the triple phase boundaries where gaseous oxygen, electrons and oxide-ions meet. Many experiments have proved that the surface diffusion of oxygen ions and ionic transfer across the electrode/electrolyte interface could be rate-limiting steps of overall oxygen reduction process. The ionic transfer process is thermally-activated with a fairly high activation energy (1 ~ 2 eV). Therefore, lowering cell operating temperature could dramatically reduce the catalytic activity of the oxygen reduction.

Mixed electronic and oxide-ion conducting perovskites are one class of materials that are actively studied as electrodes in recent years. This type of material generally contains cobalt on the B-site of a perovskite ABO₃. The perfect energy level of Co⁴⁺/Co³⁺ redox couple provides a very high electronic conductivity accompanying with appreciable oxide-ion conductivity at elevated temperatures. Conduction of both electrons and oxide-ion through crystal lattices as an entity represents one of the important features of these mixed conductors. By using them as the electrode materials, the oxygen reduction is no longer confined at the triple phase boundaries as in the case of doped LaMnO₃. In fact,
the reaction expands to all the bulk volume of the electrode. Under this circumstance, porosity in the air-electrode may not be a crucial factor any more. The oxygen exchange at the gas-solid surface was shown instead of being the rate-limiting step, a process that has a much lowered activation energy. Thereby, the overall rate of oxygen reduction is considerably accelerated, especially at lower temperature ranges. Very good electrode performance has been experimentally observed in the system La$_{1-x}$Sr$_x$CoO$_{3-\delta}$\cite{20}. Several other systems such as La$_{0.8}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$\cite{21, 22} and La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Ni$_{0.2}$O$_{3-\delta}$\cite{23} have also been suggested as the potential cathode material.

Although mixed conducting electrodes exhibit excellent electrochemical performance, their practical application as an air-electrode in a SOFC is still limited due to their exceptionally high thermal expansion coefficients (TECs) than those of electrolyte materials. This property is mainly caused by a dramatic loss of lattice oxygen at elevated temperatures. It would be very difficult to implement these mixed conductors in a practical SOFC until this issue is addressed. On the other hand, these mixed conductors have also been shown to have a greater tendency to react with the electrolyte than those of electronic conductors currently used in SOFCs.

The question to ask now is: Can we find a practical mixed conductor for low-temperature SOFCs. The answer is positive. The mixed conductivity can be created either in a homogenous phase as in the case of La-cobaltites where electrons and oxide-ions conduct simultaneously in homogenous phase and or in a dual phase where electrons and oxide-ion conduct simultaneously in discrete phases. Since there is no oxygen loss associated with the individual phases in composite mixed conductors, the thermal expansion match between the electrode and the electrolyte can be adjusted essentially by the ratio of the oxide phase. Practically, popular anode cermet and cathode interlayer materials are the examples of dual-phase mixed conductors. The literature strongly suggests that application of a dual-phase mixed conducting interlayer at the interface of the electrode and electrolyte is a viable solution for enhancing low-temperature performance of a SOFC without encountering the thermal expansion mismatch problem.

1.4 Anode Materials

Ni-based cerments are widely used and one of successful anodes in a SOFC. The excellent catalytic activity on fuel oxidation provided by nickel particles and matched thermal expansion provided by the YSZ skeleton assure an excellent performance. Recently, several studies\cite{24, 25} have shown that the performance of anode cermet can be further improved by replacing YSZ with doped CeO$_2$, particular in low-temperature range. The low-temperature enhancement benefits mainly from the mixed conductivity shown by the redox couple Ce$^{4+}$/Ce$^{3+}$ in reducing atmospheres, which catalyzes fuel oxidation. This is supported by the result of an independent catalytic study of hydrocarbon oxidation on the CeO$_2$ surface\cite{26}, which the authors concluded that CeO$_2$ is a good catalyst for complete oxidation of hydrocarbon fuels. As with most mixed conductors, doped CeO$_2$ also exhibits a large thermal expansion with loss of oxygen at elevated temperatures and low partial pressures of oxygen. This challenge must be met before it can be successfully used in SOFCs.
1.5 Summary

Realization of low-temperature SOFC depends largely on the availability of electrolyte and electrode materials that are suitable for the low temperature application. A literature survey on oxide-ion conductors suggests that the Sr- and Mg-doped LaGaO$_3$ perovskite oxide is a strong candidate for low-temperature SOFCs. Not only is the conductivity higher than that of YSZ, but also has it a better chemical and structural compatibility with cathode. For cathode materials, mixed electronic and oxide-ion conductivity is highly desired for low-temperature applications in terms of electrochemical performance. Because of the unusually high TECs observed in single-phase mixed conductors, a dual-phase mixed conductor consisting of discrete electronic and oxide-ion conducting phases as either an interlayer or a cathode substrate could be a viable solution to achieve a high performance for a SOFC at low temperatures. For anode materials, the literature seemed to suggest that doped CeO$_2$ could be a better ceramic phase in a dual-phase anode cermet because of mixed conductivity exhibited by Ce$^{4+}$/Ce$^{3+}$ redox couple. Additional work is needed to address the TEC increase in CeO$_2$ due to loss of oxygen.
2 THERMODYNAMIC ASSESSMENTS ON THE PROPERTIES OF SELECTED ELECTROLYTE MATERIAL

2.1 Introduction

The main objective of this task is to assess the thermodynamic stability of potential low-temperature electrolyte materials selected in Task 1, namely Sr- and Mg-doped LaGaO$_3$ (LSGM). Due to the nature of La-containing perovskites, the chemical stability of LSGM ceramic powders and pellets was specifically studied in CO$_2$-containing atmospheres. Fundamental properties on LSGM were also measured.

2.2 Experimental

2.2.1 LSGM preparation

Pellets of the LSGM electrolyte with the composition suggested by the literature survey in Task 1, namely La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{3-\delta}$, were prepared via solid-state synthesis routine. Specifically, the calcined (1000$^\circ$C for 4 hours) La$_2$O$_3$, SrCO$_3$, Ga$_2$O$_3$ and calcined (1000$^\circ$C for 4 hours) MgO were intimately mixed in an agate mortar with an aid of propanol. The mixture was then pelletized and calcined at 1250$^\circ$C for 12 hours. The calcined pellets were then crushed and ground into fine particles using a vibration mill, followed by pressing bar samples and finally sintering at 1450$^\circ$C for 8 hours. The sintered bar samples have a density greater than 99% of XRD density. Electrical conductivity and thermal expansion coefficient were measured on the sintered bar samples using 4-probe technique and dilatometer from 700 to 1000$^\circ$C, respectively.

2.2.2 Molten salt technique

The molten salt method has been used in the past to synthesize a number of compounds at relatively low temperatures which otherwise require higher temperatures for conventional, solid-state synthesis. The method consists of adding requisite precursors in the required ratio to a molten salt mixture or eutectic that accelerates the kinetics of formation of the desired compound. This technique has also found successful applications in studying low-temperature phase equilibrium and low-temperature thermodynamic stability. Examples include the thermodynamic stability study on BaCeO$_3$ and SrCeO$_3$ systems and extension of the low-temperature phase diagram of the TiO$_2$-SnO$_2$ and CeO$_2$-ZrO$_2$ systems. However, the applicability of this method depends on two important requirements: (1) the material under study should be slightly soluble in the molten salt medium, and (2) the molten salt solvent should not chemically react with the material under study. In this report, we show experimental results of using this technique for studying the thermodynamic stability of LSGM. To examine the applicability of the molten salt technique to this study, we selected a medium target temperature of 450$^\circ$C in order to give a clear indication of any possible chemical reaction between the solvent and the LSGM. For this temperature, the molten-salt system KCl-LiCl that contains 41 mol% KCl and 59 mol% LiCl and has a $T_{eu}$= 355$^\circ$C was chosen. The weight ratio of molten salt to ceramic powder mixture was kept between 2:1 to 4:1. After an intimate mixing the sample was heated up to 450$^\circ$C and held for 24 to 36 hours, after which it was cooled to room temperature. The reacted mixture was then washed in DI water thoroughly to remove the salts and dried in an oven overnight. X-ray diffraction and ICP
analysis were performed on the washed and dried powders. To study the atmosphere
effect, four atmospheres were used during the reaction: dry air, 6%H₂O+air, 3%CO₂+N₂
and 6%H₂O+2.8%CO₂+ N₂.

In addition, we also tried KCl-50mol%NaCl and Na₂CO₃-44mol%K₂CO₃ systems in an
effort to eliminate possible Li-LSGM reaction. At the same time, we are able to evaluate
LSGM at 800°C without experiencing significant loss of the salt due to a higher eutectic
temperature provided by the new salt systems.

2.2.3 TGA technique

Thermal analysis is a widely used and well-suited method for studying the
thermodynamic properties of materials. This technique typically includes thermo-
gravimetric analysis (TGA), differential temperature analysis (DTA), differential scanning
 calorimetry (DSC) and thermomechanic analysis (TMA). In this study, we chose TGA to
monitor the weight gains in CO₂-containing atmospheres as an indication of interactions
between CO₂ and samples.

The TGA experiment was conducted using an in house Theta Thermal Analysis system.
This system was customized about eight years ago to meet our unique need at that time.
This computer-controlled equipment allows the weight of a sample to be monitored
under a controlled temperature and atmosphere. The oxygen partial pressure of the
atmosphere surrounding the sample is continuously measured via an in situ oxygen
sensor. Processing data such as time, temperature, weight change, flow rate of the gas
and partial pressure of oxygen are recorded by the computer through an A/D-D/A
converter. Once the desired temperatures and atmospheres are programmed, the
system is able to complete the task without an operator.

The experiment was performed at an isothermal condition with changes of atmospheres.
The target temperature was selected as 800°C, while four different atmospheres
containing various CO₂ contents were introduced into the system: dry air (~300 ppm
CO₂), 3%CO₂+N₂, 33%CO₂+N₂ and 100%CO₂. Due to the unique design of the TGA
system, a sintered pellet has to be used in the furnace in order to minimize the unwanted
buoyancy when suspended from the microbalance.

The measurement was carried on well-sintered LSGM pellets. In order to isolate the
contributions from individual oxide, a pure La₃O₉ pellet that was sintered at 1400°C for
10 hours was also studied. In addition, CeO₂ and Ce₀.₆La₀.₄O₂₋δ (LDC40) that are
potential new anode materials for LSGM-based fuel cells were investigated.

2.3 Results and Discussion

2.3.1 Properties of LSGM ceramics

The conductivity and thermal expansion coefficient of LSGM and LSM sample were
summarized in the Table 2-1. For comparison, some data of Siemens Westinghouse
WPC3 cathode and La₀.₆Sr₀.₄MnO₃ (LSM) that were made from a wet-chemical method
are also included. It is evident that LSM exhibits the closest thermal expansion match
with LSGM in addition to its higher conductivity than WPC3 air-electrode. It appears to suggest that the LSM be a better cathode material for the LSGM electrolyte.

### Table 2-1 Property comparisons between LSGM, LSM and WPC3

<table>
<thead>
<tr>
<th></th>
<th>In air</th>
<th>In N$_2$+4%H$_2$O (r. t.)</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEC (25 – 1200°C)</td>
<td>DC σ at 800°C</td>
<td>TEC (25–1200°C)</td>
</tr>
<tr>
<td>LSGM</td>
<td>11.73x10^{-6}/K</td>
<td>0.12 S/cm</td>
<td>11.71</td>
</tr>
<tr>
<td>LSM</td>
<td>11.71 x10^{-6}/K</td>
<td>180 S/cm</td>
<td>-</td>
</tr>
<tr>
<td>LSGM+LSM (1:1 vol%)</td>
<td>11.68 x10^{-6}/K</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WPC3</td>
<td>10.7 x10^{-6}/K</td>
<td>~80 S/cm</td>
<td>-</td>
</tr>
</tbody>
</table>

#### 2.3.2 Thermodynamic analysis of chemical stability of LSGM in CO$_2$-containing atmospheres

The carbonate formation of an alkaline-earth element in a perovskite oxide is a well-known phenomenon and is thermodynamically favorable at lower temperatures and high CO$_2$ atmospheres. Practically, carbonate formation is extremely detrimental for SOFC applications since the presence of carbonates on the surface of the functional materials deteriorates significantly their electrical conductivity and mechanical stability. A thorough understanding of this process is, therefore, technically important in terms of preventing it from occurring in a SOFC generator.

Sr- and Mg-doped LaGaO$_3$ perovskite (LSGM) has been identified as a potential electrolyte candidate for low-temperature SOFCs. Due to its role as an electrolyte, the LSGM will be in contact with CO$_2$-containing atmospheres on the fuel side. Therefore, the chemical stability of LSGM in such an atmosphere is of critical importance. As the first part of this study, we report a thermodynamic analysis of SrCO$_3$ formation in LSGM in CO$_2$-containing atmospheres. Following to this section, experimental results obtained with the molten salt and thermal analysis techniques are reported.

The thermodynamic data on SrCO$_3$, SrO and CO$_2$ have been well documented in the literature. The SrO-SrCO$_3$ stability domains as functions of temperature, SrO activity and partial pressure of CO$_2$, were calculated directly from the work by J. J. Lander and are shown in Figure 2-1. The SrCO$_3$ stability-domain favors low temperatures and high CO$_2$ atmospheres. Since SrO in the LSGM is in a dissolved state, its activity must be considered in the calculations. The activity of SrO in the LSGM can be simply taken as its molar fraction x=0.1 if Raoult's law is followed. Otherwise, the SrO activity can be either higher than 0.1 or lower than 0.1 depending upon whether the solid solution positively deviated or negatively deviates from Raoult's law. Considering the low SrO content in the LSGM solid solution, no significant deviation is expected in our case if the molar fraction x=0.1 is taken as the activity in the calculations. In Figure 2-1, several activities of SrO were plotted against the pure SrO for comparison. This figure shows that the stability domain of SrO expands as the SrO activity decreases. Three atmospheres are displayed in Figure 2-1, which correspond to the CO$_2$ contents in depleted fuel (85% fuel utilization, P(CO$_2$)=0.35 atm), 3% CO$_2$-N$_2$ mixture (P(CO$_2$)=0.03 atm) and dry air (P(CO$_2$)=3x10^{-4} atm). It is clear that the LSGM based cells must operate...
at temperatures above \( \sim 950^\circ C \) in order to avoid the formation of \( \text{SrCO}_3 \) in the deleted fuel atmosphere. On the other hand, no \( \text{SrCO}_3 \) would form in a dry air if the operating temperature is kept above 800\(^\circ C\). It appears that protection of LSGM from forming carbonates in a practical SOFC generator may be needed.

\[
\begin{array}{c|c|c|c|c|c}
1000/T, K^{-1} & 0.75 & 0.85 & 0.95 & 1.05 & 1.15 & 1.35 \\
\log P(\text{CO}_2), \text{ atm} & 4 & 3 & 2 & 1 & 0 & -1 \\
\end{array}
\]

![Figure 2-1 Thermodynamic stability domain of SrO-SrCO₃](image)

It is to be noted that only thermodynamic factors were considered in the above calculation. The actual carbonation process may be kinetically very slow at low temperatures.

2.3.3 Results from molten salt study

2.3.3.1 KCl-LiCl salt system

The ICP results of four samples after annealing at 450\(^\circ C\) in the KCl-LiCl salt as well as the nominal composition for LSGM electrolyte were shown in Table 2-2. It is no doubt that the starting composition of LSGM has been completely changed as a result of reacting with the salt KCl-LiCl. It appears that gallium and strontium in the LSGM have been dissolved into the salt and lost by the washing process, leading to a decrease in their individual concentration. As a consequence, the lanthanum and magnesium concentrations were elevated. It is to be noted that the resulting La, Sr, Ga and Mg concentrations would depend on how well the annealed mixture was cleaned. The fluctuation of analysis data in Table 1, therefore, would not be a surprise. The compound \( \text{LaOCl} \) was detected by x-ray diffraction and confirmed the presence of Cl in the final powders. A small amount of K observed in the powders is believed to originate from the residual salt whereas the higher remaining Li content may indicate a possible formation of a Li compound with LSGM. However, this was not picked up by x-ray diffraction. All other impurities originated from the starting electrolyte LSGM, the \( \text{Al}_2\text{O}_3 \) reaction boat

22
and the salt KCl-LiCl. No effects from the atmospheres can be concluded due to the present chemical reaction between the LSGM and the salt.

Table 2-2 ICP analysis results and nominal composition of LSGM electrolyte

<table>
<thead>
<tr>
<th>Sample Elements</th>
<th>Dry air Wt%</th>
<th>3%CO₂+N₂ Wt%</th>
<th>3%H₂O+air Wt%</th>
<th>6%H₂O+2.8%CO₂+N₂, Wt%</th>
<th>Nominal composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>61.72</td>
<td>58.98</td>
<td>70.43</td>
<td>63.21</td>
<td>45.45</td>
</tr>
<tr>
<td>Sr</td>
<td>3.33</td>
<td>4.77</td>
<td>1.89</td>
<td>5.51</td>
<td>7.17</td>
</tr>
<tr>
<td>Ga</td>
<td>12.24</td>
<td>12.23</td>
<td>8.76</td>
<td>10.24</td>
<td>23.67</td>
</tr>
<tr>
<td>Mg</td>
<td>2.15</td>
<td>1.99</td>
<td>2.37</td>
<td>2.18</td>
<td>1.69</td>
</tr>
<tr>
<td>O</td>
<td>16.44</td>
<td>16.98</td>
<td>15.20</td>
<td>15.39</td>
<td>21.02</td>
</tr>
<tr>
<td>K</td>
<td>0.04</td>
<td>0.06</td>
<td>0.04</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>Li</td>
<td>0.88</td>
<td>1.26</td>
<td>0.37</td>
<td>0.18</td>
<td>-</td>
</tr>
<tr>
<td>Leachable Cl</td>
<td>2.70</td>
<td>3.20</td>
<td>0.67</td>
<td>0.95</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>0.09</td>
<td>0.10</td>
<td>0.05</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0.03</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ga</td>
<td>0.08</td>
<td>0.25</td>
<td>0.12</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>0.03</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>0.12</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis results of the above four samples are shown in Table 2-3. It is evident that a substantial amount of LaOCl was found in the final powders, implying a chemical reaction between La₂O₃ and the Cl-containing salt. As a result of this reaction, the nominal composition of the LSGM was altered, leading to a formation of second phase SrLaGaO₄.

Table 2-3 X-ray diffraction quantitative analysis results

<table>
<thead>
<tr>
<th>Phases</th>
<th>Dry air vol%</th>
<th>3%CO₂+N₂ vol%</th>
<th>3%H₂O+air vol%</th>
<th>6%H₂O+2.8%CO₂+N₂, vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaOCl, tetragonal</td>
<td>58.6</td>
<td>63.6</td>
<td>67.3</td>
<td>47</td>
</tr>
<tr>
<td>SrLaGaO₄, BCC tetra.</td>
<td>6.7</td>
<td>6.6</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>LaGaO₃, orthorhombic</td>
<td>34.7</td>
<td>29.8</td>
<td>31.8</td>
<td>52.1</td>
</tr>
</tbody>
</table>

2.3.3.2 KCl-NaCl system

A XRD pattern after reaction in air in KCl-NaCl system was shown in Figure 2-2. Different from KCl-LiCl system, LSGM remains unchanged before and after reaction, indicating no chemical reactions occurred between LSGM and either the salt KCl-NaCl or CO₂ (~300 ppm) from the atmosphere. Similarly, the XRD patterns of the samples after treatment in 3%CO₂+N₂ and CO₂ atmospheres were shown in Figures 2-3 and 2-4, respectively. Clearly, no detectable reactions between LSGM, CO₂ and the salt can been found.
Figure 2-2 XRD pattern of LSGM after reacting in air at 800°C

Figure 2-3 XRD pattern of LSGM after reacting in 3%CO₂+N₂ at 800°C

Figure 2-4 XRD pattern of LSGM after reacting in CO₂ at 800°C
The above results suggested that the newly selected salt KCl-50mol%NaCl is suitable for studying the chemical stability of LSGM using molten salt technique. Furthermore, LSGM is stable in CO₂-containing atmospheres, which is in agreement with the results obtained using thermal analysis technique discussed below.

2.3.3.3 \( \text{Na}_2\text{CO}_3-\text{K}_2\text{CO}_3 \) system

A XRD pattern of LSGM powders after reacting with \( \text{Na}_2\text{CO}_3-\text{K}_2\text{CO}_3 \) salt in 3% CO₂+N₂ at 800°C was shown in Figure 2-5. No change was found for LSGM pattern before and after the reaction, implying no chemical reactions occurred between LSGM and either the \( \text{Na}_2\text{CO}_3-\text{K}_2\text{CO}_3 \) or CO₂ from the atmosphere. Similarly, a XRD pattern of LSGM powders after treatment in 100% CO₂ atmosphere is shown in Figure 2-6. Again, no detectable reaction products between LSGM, CO₂ and the salt can be found from the XRD pattern.

![Figure 2-5 XRD pattern of LSGM after reacting in air at 800°C](image1)

![Figure 2-6 XRD pattern of LSGM after reacting in 3%CO₂+N₂ at 800°C](image2)
2.3.4 Results from TGA study

The weight changes of a LSGM pellet \((\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.87}\text{Mg}_{0.13}\text{O}_{2.815})\) were recorded as a function of time in different atmospheres at 800°C in Figure 2-7. No weight gains up to 3% CO\(_2\) can be found at this temperature. This observation agrees well with the theoretical calculations shown in Figure 2-1. Appreciable weight gains were seen when a gas containing CO\(_2\) content greater than 33% was introduced into the furnace. However, the absolute values were found to be much smaller than those predicted \((0.002\% \text{ vs } 13.5\% \text{ for } 33\% \text{ CO}_2 \text{ composition})\) from assuming carbonation of lanthanum and strontium in LSGM. The dramatic difference implies the kinetics of the actual carbonation process are effectively limited at the sample surface due to a well-sintered dense ceramic body (The density of the pellet was measured to be 99% of the theoretical value). Another observation of Figure 2-7 is that the carbonation process is kinetically reversible upon CO\(_2\) changes.

![Figure 2-7 TGA curve of LSGM ceramics](image)

Figure 2-8 presents a similar measurement on the sample of Ce\(_{0.6}\text{La}_{0.4}\text{O}_{1.80}\) (LDC40) that is intended to be used as an anodic interlayer material for protection of LSGM from reacting with Ni and promotion of anodic electrochemical reactions. A significant weight loss upon heating is certainly due to the loss of oxygen that results from the reduction of Ce\(^{4+}\) to Ce\(^{3+}\) at elevated temperatures. Again there were no appreciable weight gains up to 3% CO\(_2\), after which approximately 0.005% and 0.012% weight gains were observed for 33%CO\(_2\) and 100%CO\(_2\), respectively. These values are far less than that of predicted, i.e., 12% for 33% CO\(_2\) composition assuming cerium and lanthanum are both carbonated. As stated above, this big difference is a result of the limited kinetics on the surface by the well-sintered ceramic body. Similarly, Figure 2-8 shows a reversible behavior upon switching off CO\(_2\).

---

\(^1\) A depleted fuel contains typically 33%CO\(_2\)
Figure 2-9 shows the weight changes of a La$_2$O$_3$ pellet as a function of time in different atmospheres at 800°C. As expected, there were essentially no weight gains up to 3%CO$_2$ at this temperature, after which approximate 0.04% weight gain in 33% CO$_2$ stream were observed. This finding agrees with the results shown in Figure 2-7. Dramatic weight gains were clearly seen when a 100% CO$_2$ stream was introduced into the system. The absolute values were found to be much larger than those of LSGM reported in Figure 2-7 (8.5% vs 0.017%), but still less than the theoretical value of 40.5%. It appears from Figure 2-9 that the carbonate formation process did not complete before the CO$_2$ was cut-off. However, it is reasonable to postulate that all La$_2$O$_3$ would be carbonated if sufficient exposing time were allowed. Since the formation of lanthanum carbonate is thermodynamically favorable in CO$_2$ atmosphere at 800°C, the presence of large cracks on the surface of La$_2$O$_3$ certainly promotes the kinetics of the carbonation process.

The weight changes of CeO$_2$ in CO$_2$-containing atmospheres at 800°C, Figure 2-10, showed much smaller weight gains and very similar characteristics to that of LDC40 shown in Figure 2-8. Approximate 0.004% and 0.011% weight gains were found on 33%CO$_2$ and 100%CO$_2$ stream, respectively. These values are far less than those predicted from theoretical calculations, indicating that the carbonate- formation process was primarily limited on the sample surface. Upon cutting-off CO$_2$, the formed carbonates decomposed into the oxide.

---

$^2$This value was extracted from the data recorded by the TGA system. It is difficult to distinguish the difference due to the large scale of Fig. 1.
Figure 2-9 TGA curve of pure La$_2$O$_3$

Figure 2-10 TGA curve of pure CeO$_2$
2.4 Summary

Extensive reactions occurred between the electrolyte LSGM and solvent KCl-LiCl at 450°C regardless of what the gas composition of atmosphere used for the tests. This finding suggests that the molten salt method is not applicable to the thermodynamic study on LSGM. In addition, the test temperature (450°C), which is based on the melting temperature of the selected salt, does not match the SOFC operating temperature 800°C for LSGM electrolyte. In contrast, the newly selected salt Na₂CO₃-44mol%K₂CO₃ and NaCl-50mol%KCl system were found not to react with LSGM and suitable for studying the chemical stability of LSGM using molten salt technique. The results clearly showed that LSGM is chemically stable in CO₂-containing atmospheres.

LSGM, LDC40 and CeO₂ appeared to show carbonates formation at 800°C in an atmosphere containing greater than 33% CO₂. A considerable difference in weight gains between the measured and calculated values suggests the carbonation process is most limited to a thin layer on the sample surface. The carbonation process is reversible and the formed carbonates are removable upon removal of CO₂. Whether the formation of this thin layer of carbonate affects the electrical performance of a cell is subject to the cell testing. However, it is worth to mention that there is no visual difference in the sample before and after TGA measurement.

In contrast, La₂O₃ showed carbonates formation at 800°C in an atmosphere containing greater than 33% CO₂. A considerable weight gain on a cracked La₂O₃ sample reconfirmed the conclusion that the carbonation process is most limited to the sample surface. Post-test examinations on the TGA samples reveal very brittle characteristics in La₂O₃ sample, indicating a significant carbonate formation.
CHEMICAL COMPATIBILITY OF ELECTROLYTE AND CATHODE SUBSTRATE

3.1 Introduction

High temperature reactivity between LSGM and cathode substrate has long been a concern during fabrication of thin-film LSGM fuel cells. Despite no insulating phases such as zirconate that is commonly found in ZrO$_2$-based fuel cells are expected to form, interdiffusion between Ga-Mn could potentially alter the chemistry of LSGM electrolyte, which could lead to formation of secondary less-conductive phases. Therefore, study of chemical compatibility of LSGM with LaMnO$_3$-based cathode is important in making thin film LSGM based fuel cells and is a major task of the project.

3.2 Experimental

Slurry dip-coating technique was used to make LSGM electrolyte thin-films on SWPC tubular cathode substrate. The slurry was prepared with a proprietary formula that is based on propanol as the solvent. The LSGM-slurry was dip-coated on 3"-long tubular segments, which include two types of porous tubes: Bisque Fired (BF) and Fully Fired (FF), either in standard or fine-grained microstructure. The coated tubes were then sintered at 1450, 1475, and 1500°C for 3 hours to study the temperature effect. The sintered tube-segments were then subject to window leak rate test as well as submitted for microanalysis.

Window leak rate in mmHg/min was measured using a home made setup, by which a defined area of electrolyte surface was capsulated and the vacuum leak rate was measured as a function of time.

EBMA (Electron Beam Microanalysis) technique was used to examine the change in chemical composition across the interface of LSGM and cathode-substrate after high temperature densification.

3.3 Results and Discussion

The window leak rate results of co-sintered LSGM films on cathode substrates were listed in Table 3-1. It is evident that bisque-fired WPC3 tubes allowed densification of LSGM films more easily than fully-sintered tubes. On the other hand, fine-grained tubes have a better chance to yield dense LSGM films than standard tubes. Microstructural examinations agreed well with the window leak rate test, see Figure 3-1 below. The results seem to indicate the importance of maintaining the closest co-shrinkage rate during sintering of films and substrates in order to achieve the highest film density. It is to be noted that retention of the porosity required for adequate oxygen diffusion in the WPC3 tube has not been considered at the present stage.

| Table 3-1 Window leak rate (mmHg/min) of co-sintered LSGM electrolyte on SWPC substrates |
|-----------------------------------|----------|----------|----------|
| BF STD WPC3 | 1450°C | 1475°C | 1500°C |
| FF STD WPC3 | leaky | 45 | 0.3 |
| BF FG WPC3 | leaky | - | 70 |
| BF FG WPC3 | leaky | 0.3 | 0.1 |
The microstructures of co-sintered LSGM films on SWPC substrates were examined primarily using optical microscopy after the samples were well polished. Figure 3-1 shows the microstructures of co-sintered LSGM films on substrates as a function of sintering temperature. At 1450°C, Figure 3-1(a), the LSGM film on the BF-standard (STD) substrate was seen to have a porous microstructure with an appearance of the second phase that is dark in color. Similarly, Figure 3-1(b) revealed a LSGM microstructure on the fine-grained (FG)-BF substrate, but with a developing dense layer at the interface that is bright in color. The porous structures confirmed the high window leak rate shown in Table 3-2. With increasing sintering temperature to 1475°C, Figure 3-1(c), the LSGM film on the BF-STD substrate appeared to consist of two layers, one on the top similar to Figure 3-1(a) and another dense one growing from the interface. The growth of the dense layer appeared to complete as indicated by disappearance of top porous layer in the LSGM film on the FG substrate, see Figure 3-1(d). With further increasing the sintering temperature to 1500°C, both BF-STD and BF-FG supported LSGM films were shown to become dense in Figures 3-(e) & (f), respectively. No top porous layer that contains second phase was visible any more at a temperature ≥1500°C. This observation suggests that the second phase is either dissolved by the growing dense layer or simply vaporized. In this aspect, determination of chemistry across the interface is necessary.

As pointed out above, the un-densified electrolyte layer typically contains two phases. Figure 3-2(a) and (b) show a back-scattered SEM micrograph and the corresponding EBMA line scan across a LSGM layer on an FS-STD substrate. The A/B ratio was close to 1 across the region from 0 to 40 μm, indicating a perovskite structure in both the LSGM electrolyte layer and the substrate. At ~50 μm where a dark phase is located, EBMA revealed an A/B ratio close to 2/3. This finding infers that the dark phase has a formula of A₂B₃O₇ that is commonly found in LSGM-based materials. The compositions for the major ABO₃ and minor A₂B₃O₇ (denoted as 237) phases are averaged to be 

\[
\begin{align*}
&\text{La}_{0.88}\text{Sr}_{0.07}\text{Ce}_{0.03}\text{Ga}_{0.61}\text{Mn}_{0.27}\text{Mg}_{0.10}\text{Cr}_{0.02}\text{O}_{3-δ} \\
&\text{La}_{1.04}\text{Sr}_{0.52}\text{Ca}_{0.41}\text{Ce}_{0.02}\text{Ga}_{2.95}\text{Mn}_{0.03}\text{Mg}_{0.02}\text{O}_{7-δ}
\end{align*}
\]

Clearly, a significant Ga-Mn interdiffusion has occurred across the LSGM and WPC interface during high temperature densification whereas Ce, Ca and Cr contents in the perovskite phase are very small. However, plenty of Ca were found dissolved in the 237 phase with Ce, Mn and Mg as minor components, in contrast to the commonly found impurity LaSrGa₃O₇. It appears that Mn and Ca diffuse preferentially into the LSGM perovskite and 237 phase, respectively, with the counter diffusion of Ga and Sr into the WPC substrate, see Figure 3-2(c).

Typically, a dense LSGM layer is frequently found with a single-phase composition. This was illustrated in Figures 3-3(a) and (b), which showed an LSGM layer co-sintered on a BF-STD substrate. EBMA line scan, Figures 3-3(b) and (c), revealed the composition 

\[
\begin{align*}
&\text{La}_{0.87}\text{Sr}_{0.07}\text{Ce}_{0.04}\text{Ca}_{0.04}\text{Ga}_{0.60}\text{Mn}_{0.26}\text{Mg}_{0.08}\text{Cr}_{0.02}\text{O}_{3-δ} \\
&\text{La}_{0.87}\text{Sr}_{0.07}\text{Ce}_{0.04}\text{Ca}_{0.04}\text{Ga}_{0.60}\text{Mn}_{0.26}\text{Mg}_{0.08}\text{Cr}_{0.02}\text{O}_{3-δ}
\end{align*}
\]

for LSGM layer, which is essentially identical to that of LSGM on a fully sintered WPC substrate. The absence of the impurity phase 237 in the LSGM layer for the bisque-fired SWPC substrate is surprising, implying that a close relationship between co-shrinkage of film-substrate and cation interdiffusion at elevated temperatures could be existent. To understand this relationship, the sintering mechanism of LSGM needs to be better clarified. The precursor LSGM slurry used for dip coating was made from LSGM powders that were calcined at 1250°C for 12 hours. X-ray diffraction revealed a three-phase mixture of sub-stoichiometric perovskite...
(LSGM), LaSrGa\(_4\) (denoted as 214) and LaSrGa\(_3\)O\(_7\). At higher temperatures (typically \(>1450^\circ\text{C}\)) the sub-stoichiometric perovskite reacts with LaSrGaO\(_4\) and LaSrGa\(_3\)O\(_7\), resulting in the desired single-phase perovskite LSGM. The shrinkage of LSGM during the sintering is usually accompanied by the disappearance of impurity phases LaSrGaO\(_4\) and LaSrGa\(_3\)O\(_7\). This dissolution process can be expressed as follows:

\[
\text{La}_{1-x-q-r}\text{Sr}_{x-q-r}\text{Ga}_{1-q-3r-y}\text{Mg}_y\text{O}_{3-0.5(x+y)-4q-7r} + q \text{LaSrGaO}_4 + r \text{LaSrGa}_3\text{O}_7 = \text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-0.5(x+y)}
\]

However, the scenario is quite different when other cation-diffusion sources are present during the sintering. The dissolution of 214 and 237 phases into the perovskite phase could be hindered or altered by these foreign cation diffusions. With a fully-sintered WPC3 as a substrate, for example, the sintering shrinkage of LSGM layer may be dragged by the rigid substrate, leading to a porous film structure and incomplete dissolving of second phase, namely 237. As a result, the Ca-diffusion outpaces the dissolving process, producing Ca-containing 237 phase as shown in Figure 3-2(b). In contrast, when the shrinkage of LSGM film is bettered matched with that of the bisque-fired substrate, the dissolution process of 214 and 237 phases is fast enough to complete prior to Ca-diffusion into the 237 phase. This would lead to a single perovskite phase composition in the LSGM layer as shown in Figure 3-3(b).

3.4 Summary

The formation of perovskite LSGM film on the SWPC cathode substrate is a kinetics-related process. Therefore, it must be very sensitive to the sintering temperature and duration. The co-shrinkage of LSGM film and the underlying substrate is critical to achieve higher density of LSGM film. However, considerable chemical interdiffusion between Ga and Mn was found after sintering the film above 1400\(^\circ\text{C}\). The interdiffusion altered the true chemistry of LSGM, which in turn results in formation of second phases inside LSGM matrix. Lowering sintering temperature of LSGM film is, therefore, the key for the success of LSGM fuel cell development.
Figure 3-1 Microstructures of co-sintered LSGM films on various SWPC substrates
Figure 3-2 LSGM (1250°C/15hrs) film co-sintered at 1500°C/3hrs on the fully sintered WPC substrate. (a) Back-scattered image (b) A/B ratio variation with distance (c) Elemental distribution over distance.
Figure 3-3 LSGM (1250°C/15hrs) film co-sintered at 1500°C/3hrs on the bisque-fired WPC substrate. (a) Back-scattered image (b) A/B ratio variation with distance (c) Elemental distribution over distance.
4 ELECTROCHEMICAL CHARACTERIZATIONS ON LSGM-BASED CELLS

4.1 Introduction

The objective of this task is to electrochemically characterize LSGM-electrolyte/electrode interfaces using AC impedance and DC polarization techniques. The results from this study will provide useful information for selecting low-polarization electrode materials for low-temperature LSGM-based fuel cells.

4.2 Experimental

4.2.1 LSGM powder making

LSGM (La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$) powder was made from solid state reaction of a mixture containing La$_2$ (CO$_3$)$_3$•xH$_2$O, SrCO$_3$, Ga$_2$O$_3$, and MgO. La$_2$ (CO$_3$)$_3$•xH$_2$O was initially determined to be 7.71 moles to 1 mole of La$_2$(CO$_3$)$_3$. Powders were mixed in appropriate stoichiometric ratios and milled with Zirconia milling media for 24 hours, followed by calcining at 1200°C in air for 4 hours. The pre-calcined powder was then ball-milled, pelletized, and sintered at 1450°C for 10 hours. X-ray diffraction analysis of the powder (not shown here) confirmed a single-phase perovskite.

4.2.2 LSM (La$_{0.9}$Sr$_{0.1}$MnO$_3$) powder making

La$_2$(CO$_3$)$_3$•xH$_2$O (99.9%), SrCO$_3$ (99%), MnO$_2$ (99.9%) were used as starting materials. The intimate mixture was calcined at 1200°C in air for 4 hours. XRD pattern confirmed a single-phase material. The as-calcined powder was further ground into fine particle size (1-3 µm) with zirconia balls in methanol for 36 hours.

4.2.3 LSCF (La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_3$) powder making

The same procedure as LSGM and LSM powder making was used for making LSCF. After 36-hour ball milling, the particle size was reduced to the range of 0.226 µm to 4.472 µm, which is suitable for electrochemical experiments.

4.2.4 LSM + LSGM (50wt%-50wt%) powder making

A mixture of LSM and LSGM in a ratio of 50:50 (wt%) was ball-milled for 24 hours. The mean particle size was 1.19 µm with a range from 0.15 µm to 6.72 µm.

4.2.5 Preparation of electrochemical cells

The fully dense La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ (LSGM) electrolyte pellet was carefully ground to a 1.5 mm in thickness. Scotch tape was used as the mask to create ‘un-electroded’ rings around the LSCF electrodes.

The fine electrode powders (LSM, LSCF and LSM+LSGM) were dispersed in a 99.9% pure ethylene glycol solution and the weight ratio (solvent to powder) was kept as 1:1. The slurries were intimately mixed and agitated in an ultrasonic bath. Then the masked...
pellet was immediately dipped into the slurry. After soaking for 30 seconds, the pellet was slowly pulled out and dried at room temperature for about 5 hours. The mask was then peeled off and the samples (LSGM pellet with electrode coatings) were fired in air at 900°C for 1 hours. The above steps were repeated several times to achieve the desired coating thickness (25 – 30 µm).

For Pt-electrode cell, a commercial Pt paste was used to coat on both surfaces of LSGM pellet, followed by curing in air at 800°C for 30 minutes.

Finally, two very small pieces of platinum mesh were spot-welded to platinum wires and attached to the electrode coating by spring loading to serve as the current collectors.

4.2.6 AC impedance measurement

The aforementioned test cell was placed in the hot zone of a vertical furnace and air was fed directly to both electrode surfaces through two small mullite tubes. The tests were carried out over a temperature range from 600 to 800°C with an interval of 50°C. At each fixed temperature, AC impedance spectroscopy were taken in the frequency range from 0.001 Hz to 65 kHz with an AC amplitude of 10 mV.

4.2.7 DC polarization measurement

V-I measurements were potentiostatically taken on the same cell from 0 to 1.0 V and back to 0 in steps of 0.2 V. At each point, the voltage was held for 30 minutes to ensure a true stabilization.

4.3 Results and Discussion

4.3.1 Electrical conductivity of bulk LSGM

The conductivity of a fully dense LSGM pellet was measured in air over the temperature range 600 - 800°C by the four-probe DC and two-probe AC impedance methods.

The electrical conductivity of LSGM are summarized in Table 4-1. For comparison, the conductivity from Goodenough et al. are also shown. At lower temperatures (600 - 700°C), the conductivity from DC and AC measurement are almost the same. However, at higher temperatures (700 - 800°C), the results from AC measurement are lower than that of DC measurement, which is consistent with the results of the symmetric electrode experiments. AC method is in principle able to measure the bulk conductivity whereas DC measures the total (bulk and grain boundary) conductivity. At higher temperatures, grain boundary effects become increasingly important, which departs the data obtained from AC and DC methods.

| Table 4-1 Electrical conductivity $\sigma$ (s/cm) of LSGM |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|
|                                | 600°C          | 650°C          | 700°C          | 750°C          | 800°C          |
| DC measurements                | 0.016          | 0.023          | 0.0418         | 0.0726         | 0.11           |
| AC measurements                | 0.016          | 0.026          | 0.0418         | 0.0567         | 0.0632         |
| Goodenough et al.              | 0.015          | 0.05           | 0.12           |                |                |
4.3.2 Pt electrode

A representative AC impedance spectrum of LSGM sample with Pt electrode was shown in Figure 4-1 (a). The high frequency intercept represents the ionic conductivity of LSGM, which was listed in Table 4-1 whereas the arcs between high-frequency and low-frequency are indications of electrode resistance. The shown reduced electrode resistance by applied cathodic DC bias implies that charge-transfer process play an important role in the electrode kinetics of Pt/LSGM interface.

![Figure 4-1 (a) AC impedance spectra measured at 800°C in air and (b) DC polarization curves at various temperatures with Pt electrode](image)

The V-I characteristics of the same cell was also measured and shown in Figure 4-1 (b). As expected, the DC polarization decreases with temperature, but with an appearance of curvature. The non-linearity of V-I curve indicates the polarization enters into “strong” polarization field. However, the overall DC current is relatively small, implying a high interfacial resistance. Post-test examination revealed the detachment of Pt-mesh, which could contribute to the observed high resistance.

4.3.3 LSCF electrode

Figure 4-2 (a) showed impedance spectra with LSCF electrode at various temperatures. Generally speaking, both high-frequency and low-frequency resistances were reduced as the temperature increases. However, in comparison with Pt-electrode, Figure 4-1 (a), the overall electrode resistances at all temperatures were considerably reduced. This observation indicates that LSCF is a better electrode for oxygen reduction than Pt-electrode.
The V-I curves measured from 600 to 800°C in air were also shown in Figure 4-2 (b). Different from Pt-electrode, Figure 4-1 (a), the LSCF electrode generated V-I curves more linear at high temperature than at low temperature. This observation makes a lot sense because the electrode tends to become more reversible with reduced polarization as temperature increases. At 600°C, an apparent curvature was found, indicating a strong polarization. An attempt of using Tafel equation to fit the experimental data was illustrated in Figure 4-3, where equation $V = a + b \ln(i) + iR$ was used. From the curve fitting the system ohmic resistance $R$ was obtained and the exchange current density $i_0$ was calculated from $i_0 = \exp(-a/b)$. It was found that the exchange current density at 800°C is almost 25 times higher than that at 600°C.

4.3.4 LSM+LSGM electrode

The relatively high high-frequency and low-frequency resistances with LSM+LSGM electrode shown in Figure 4-4 (a) indicate a possible bonding problem between LSGM+LSM and LSGM interface, and poor electrochemical performance offered by this particular composite electrode. However, this observation does not necessarily mean LSGM+LSM system is inadequate for LSGM fuel cells. In turn, it may imply that the electrode was poorly prepared. One evidence of this speculation is that mass transportation limitation occurs at 600°C, i.e., indicating a dense electrode microstructure.
Correspondingly, the V-I curves shown in Figure 4-4 (b) indicated a high polarization with curved characters. In overall, the cell current is much smaller compared with Pt and LSCF electrodes for a given voltage.

Figure 4-3  The 600°C V-I curve fitting with the equation \( V = a + b \ln(i) + iR \)

Figure 4-4 (a) AC impedance spectra and (b) DC polarization curves measured from 600 to 800°C with LSM+LSGM electrode
4.4 Summary

The electrochemical characterizations on LSGM/cathode (Pt, LSCF and LSM+LSGM) interfaces were conducted in air from 600 to 800°C on symmetrical cells with AC impedance and DC polarization techniques. The results clearly suggested that LSCF has the lowest polarization among the three electrodes studied and is most suitable for use as a cathode material for LSGM-based fuel cells in terms of electrochemical performance.
5.1 Introduction

Development of a plasma-spray process for manufacturing LSGM-based fuel cells is an add-on task of the original program. The rationale of proposing plasma spray technique is mainly based on two considerations. First, the results in Task-3 strongly suggested that LSGM would react extensively with LaMnO$_3$ via solid state diffusion at above 1400°C and in air. Second, the green density of plasma-sprayed layers is generally high, which enables low-temperature post-spray heat treatment and ensures a minimum potential chemical reaction. The objective of this task is to explore the viability of fabricating LSGM thin-films on tubular cathode substrate using plasma spray technique.

5.2 Experimental

5.2.1 Synthesis of plasma sprayable LSGM powders

Both conventional solid state reaction and Pechini methods were used to synthesize LSGM powders. The former involved intimate mixing component oxides and carbonate, followed by calcinations at 1250°C for 12 hours and final sintering at 1450°C for 10 hours. Thus made ceramic powders were further ground into fine particles for either subsequent spray drying or air-classification to achieve flow property for plasma spray operation. The latter involved dissolving component nitrates into DI water, followed by adding citric acid and ethylene glycol to form chelated resin. The formed resin was then charred and decomposed in air at 1000°C for 8 hours. The obtained powders were then further ball-milled to break up soft agglomerates, and ready for spray-drying to make agglomerates.

The trials of spray-drying LSGM powders were conducted in SWPC with a recipe chosen from another study. The spray-drying operation used Yamoto GB-22 mini-spray drier with a nuzzle pressure of 0.5 kg/cm$^2$, air flow of 0.30 m$^3$/min and a slurry-feeding rate of 10 mL/min.

In addition, synthesis of LSGM powders using plasma spray technique was also tried in US Nanocorp.

5.2.2 Synthesis of LDC40 (La$_{0.4}$Ce$_{0.6}$O$_{1.8}$) powders

LDC40 is designed to serve as a diffusion-barrier material for anode to prevent potential chemical reaction between LSGM and Ni. A total of 20 kg LDC40 powder was synthesized using Pechini method. The following steps describe the procedures for making LDC40 powders.

1. 1030.88g La(Ac)$_3$•1.5H$_2$O was dissolved with the aid of mechanical stirring in 7 liter de-ionized water in a stainless steel pot to make solution A.
2. 1546.68g Ce(NO$_3$)$_3$•6H$_2$O was added to solution A. It dissolved quickly with mechanical stirring, resulting in solution B.
3. Solution B was filtrated to remove any dirt.
4. 1711.88g citric acid was dissolved in 1 liter de-ionized water.

5. Citric acid solution was added into solution B to complete chelating reaction. White fibrous precipitation was observed as citric acid solution was introduced, it was then disappeared as more citric acid solution was added, resulting in clear chelated solution. The solution was stirred for another 30 minutes.

6. Then, 553.04g ethylene glycol was added into the chelated solution and stirred for 30 minutes.

7. The above solution was then transferred to four glass trays and heated in an oven at 150°C for 12 hours.

As an alternative, plasma spray technique was also used for synthesizing 2-kg batch of LDC40.

5.2.3 Plasma spraying LSGM electrolyte layers

The LSGM electrolyte layers were deposited by plasma spray technique on SWPC’s cathode substrates. The LSGM powder used was purchased from Praxair, which has a composition of La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} with a purity of 99.9% and particle size distribution of 31.7µm/D_{10}, 36.9µm/D_{50} and 44.0µm/D_{95}. The flow ability is satisfactory at the feeding rate used in the tests. The reason for using commercial materials is two-fold (1) to gain practical experience in thermally sprayed electrolyte; (2) to use commercial powder as a baseline comparison.

The plasma spray operation was performed using Metco 4NB system with an external powder feeding mechanism. The system is equipped with a robotic arm and turntable. A particular assembly structure is schematically shown in Figure 5-1.

The plasma spray parameters used for LSGM film deposition were optimized through an extensive study. The selected condition for this work is as-followed:

- **Primary gas**: Ar, 150 scfh/100 psi
- **Secondary gas**: He, 180 scfh/50 psi
- **Gun power**: 35 kW (53 V @ 650 A)
- **Standoff distance**: 3.5 inches
- **Gun transverse speed**: 1,000 mm/s
- **Gun vertical index**: 2 mm/s
- **Powder feed rate**: 2 lbs/hour

5.2.4 Plasma spray of LDC40 interlayer and porous LDC40+NiO anode

The thickness of LDC40 interlayer is expected to be less than 10µm. In normal plasma spray process using powder as a feedstock, it is quite difficult to obtain such thin layer with a uniform thickness. Liquid feedstock thermal spray (LFTS) technique was proposed and tried to deposit LDC40 thin film. The results indicated that a thin LDC40 layer with a thickness less than 10 µm can be coated on the top of LSGM layer as well a stainless steel substrate. Regular plasma spray was used to make porous LDC40+NiO anode layer, but with a much lowered power level.
5.2.5 Gas leakage test

Gas leakage tests have been performed on specimens including an as-received SWPC’s cathode tube, an LSGM coated cathode tube, and a complete fuel cell single unit (consists of LSM cathode, LSGM electrolyte, LDC40 barrier layer and LDC40+NiO anode). The gas-leakage-testing device is shown in Figure 5-2, where the test pieces were assembled in between two rubber gaskets located underneath and above two plates. These two plates were tightened by two sets of bolts. The whole assembly was then immersed into ethanol and tested for gas leakage under 6 psi pressure of nitrogen. Bubbles at tube/ethanol interface were used as indication of gas leak.

![Figure 5-2 Experimental setup for gas tightness measurement](image-url)
5.2.6 Electrochemical testing of plasma sprayed fuel cells

A testing rig was built for preliminary tubular fuel cell testing. A schematic is illustrated in Figure 5-3. Gold foils were placed on both ends of the cell to serve as the seals. During operation, air and H$_2$+3%H$_2$O were fed into inside and outside of the tube, respectively. At desired temperature, the cell OCV and V-J were taken.

In addition, the impedance spectrum was also measured on a half-cell configuration, namely Pt/LSGM/cathode, in an effort to study the electrical property of plasma sprayed LSGM films.

5.3 Results and Discussion

5.3.1 Spray dried LSGM powders

Figure 5-4 (a) showed the particle morphology of LSGM powders after spray drying. The particles were seen to be spherical and averaged to be around 25 µm. This observation was further confirmed by particle size analysis, see Figure 5-4 (b). Another finding from the particle size analysis is that the particle size distribution is bimodal, which is a typical feature of free-flowing powders. The flow ability of powders measured by Hall flow meter gave an approximate 84 seconds for 50-g powder. This value is within the specification of powder required for APS operations.

5.3.2 Powder characterizations

XRD analysis was performed on the as-synthesized LDC40 and LSGM powders (wet-chemical). The data are shown in Figure 5-5 (a) and (b), respectively. It reveals a single-phase LDC40. However, wet-chemical synthesis of LSGM powders were proved to be unsuccessful. Some unknown peaks were observed in XRD patterns of the as-synthesized LSGM powders. Chemical analysis suggested a possible loss of component materials during synthesis. Starting materials used for LSGM wet-chemical synthesis include lanthanum acetate, strontium carbonate, gallium nitrate solution, and
magnesium oxide. It is speculated that MgO changed its composition during storage due to its reactivity with CO\(_2\) and H\(_2\)O in air. A heat-treatment was then performed on MgO at 1000°C. A new batch of LSGM powder using heat-treated MgO powder was again synthesized. Unfortunately, XRD pattern persisted to reveal impurity phases in the made LSGM powders. The secondary phase in LSGM powder is identified to be LaSrGa\(_3\)O\(_7\), which is in agreement with that reported in the literature.

![Particle morphology of LSGM-5nd at 200X](a)

![Size distribution of spray-dried LSGM powders](b)

**Figure 5-4** (a) Particle morphology and (b) size distribution of spray-dried LSGM powders

![XRD patterns of as-synthesized LDC40 powders and commercial LSGM powders](a)

**Figure 5-5** XRD patterns of (a) as-synthesized LDC40 powders and (b) commercial LSGM powders

5.3.3 Plasma sprayed LSGM powder

The XRD Patterns shown in **Figure 5-6** revealed a multiphase in the synthesized LSGM after plasma spray. Heat-treatments at different temperatures did not remove the impurity phases. These unwanted phases are exactly the same as those observed in the
powder prepared using wet chemistry route, inferring a possible element loss during plasma spray.

Figure 5-6 XRD patterns of as-synthesized and heat-treated LSGM powder.

5.3.4 Plasma spray LDC40 powder

Figure 5-7 showed an XRD pattern comparison of LDC40 powders made from wet-chemical and plasma spray. Due to the stable property owned by simple fluorite materials, no difference can be found between these techniques.

Figure 5-7 XRD analysis of as-synthesized LDC40 powders using different processes: (a) wet chemistry; (b) plasma spray.
Characterization on microstructures of plasma sprayed LSGM layers

Figure 5-8 showed a 120-µm thick LSGM layer deposited on SWPC’s cathode substrate by plasma spray. It is evident that the coating is generally dense in microstructure and well bonded to the substrate. However, a close look of the microstructure, Figure 5-8 (b), revealed the existence of vertical cracks with a typical dimension of 10-20 µm. It is believed that micro cracks were resulted from residual thermal stress during cooling process after plasma spray and can be mitigated by optimizing the plasma spray parameters.

An improved LSGM layer with a thickness of ~100 µm was shown Figure 5-9, where no micro cracks were visible. However, some un-melted or partially melted particle inclusions were found, which may not impose serious leakage if they stay enclosed.

Figure 5-9 Cross-section of LSGM coating made with improved plasma spray operation
A physical look of as-sprayed tube segment was shown in Figure 5-10. The leak test of this sample indicated that the LSGM film could hold up a vacuum leak rate as low as 1 torr (1 torr=$10^{-3}$ mmHg) per 1 minute.

![Image of LSGM and WPC3](image)

**Figure 5-10 Microstructure and physical look of as-sprayed LSGM electrolyte**

As mentioned earlier, the wet-chemical and plasma sprayed LSGM powders did not produce single phase material. An adjustment was made on the as-batched LSGM powder in order to compensate the material loss. Figure 5-11 showed XRD patterns of as-received and as heat-treated. A single-phase LSGM was clearly found after plasma spray. The intensity of the XRD peaks increased with annealing temperature from 500 to 800°C, indicating an increased crystallinity of as-sprayed LSGM layer. No difference in XRD patterns was found for temperatures above 800°C, which suggested that as-sprayed amorphous LSGM can be completely crystallized at above 800°C.

![Image of XRD analysis](image)

**Figure 5-11 XRD analysis of as-sprayed and heat-treated LSGM pellets.**
A cross-section of a complete set of anode-electrolyte-cathode, which consists of an LDC40 + NiO anode layer, an LDC40 interlayer, and an LSGM electrolyte layer deposited on SWPC’s cathode tube, was shown in Figure 5-12. It is difficult to discern the LDC40 interlayer due to its thin thickness. The anode layer was highly porous with a thickness of ~ 80 µm.

![Figure 5-12 Cross-section of a SOFC consisted of LDC+NiO anode, LDC40 barrier layer, LSGM electrolyte layer, and LSM substrate](image)

5.3.6 Electrochemical characterizations on plasma sprayed LSGM layers

Two different types of LSGM thick films or discs were prepared either by plasma spraying or by hydraulic pressing LSGM powders. A flat aluminum substrate was used for plasma spray and was dissolved in NaOH solution to get a self-standing LSGM film. The as-sprayed pellets were annealed in a temperature range of 500 to 1400°C and followed by a XRD characterization. The pressed pellets were sintered at 1450°C for 4 hours in air. The size of the disc was 13 mm and 9 mm in diameter with the same thickness of 550 µm for sintered one and for sprayed, respectively. Both sintered and plasma sprayed pellets were coated with Pt paste with a diameter of 9-10mm. The Pt foil was used as the current collector on both sides. The electrochemical impedance spectrum (EIS) was measured by Frequency Response Analyzer (Solartron 1250) at temperatures of 500 – 800°C in air. An LSGM layer in the thickness of 100 µm was also sprayed on SWPC’s cathode substrate.

![Figure 5-13 shows the change in impedance spectra for as-sprayed LSGM as a function of temperature ranging from 650°C to 800°C. The real portion of the complex impedance decreased significantly when temperature was over 700°C, which could be due to two contributions from temperature effect or transformation of amorphous state to](image)
crystalline one. Combining the XRD results as shown in Figure 5-11, the phase transition played an important role. The complete crystallization might occur between 700°C to 750°C that is consistent with the XRD results. After the specimen was heat-treated at 800°C for 2 hours, the impedance spectra at different temperatures were repeated and plotted in Figure 5-14 (a). Since the frequency limit (65 kHz) of the instrument, the semi-circle in the high frequency region might not be recorded in the ac complex impedance spectra. Therefore, it may be reasonable to assume that the first intersection points on the $Z_R$ axis represents the electrical resistance from the bulk. In order to confirm this assumption and to further confirm that the sprayed LSGM has the same ionic conductivity with completely crystalline LSGM, powder LSGM was pressed into pellets and sintered at 1450°C for 4 hours. The corresponding ac impedance spectra were measured for these sintered LSGM pellets shown in Figure 5-14 (b).

![Figure 5-13](image1.png)

**Figure 5-13** The AC complex impedance plot for as-sprayed LSGM during heating at temperatures of 650 – 800°C

![Figure 5-14](image2.png)

**Figure 5-14** The AC impedance spectra at different temperatures for LSGM: (a) sprayed and heat-treated at 800°C, (b) pellets sintered at 1450°C.
By comparing Figure 5-14 (a) and (b), it can be seen that the high-frequency intersection at real axis between sprayed and sintered LSGM are almost same, which implies a close conductivity between two samples. A detailed comparison was given for the impedance spectra between sprayed and sintered LSGM at 800°C in Figure 5-15. A value of 0.75 and 0.82 $\Omega$ can be read in the figure for the bulk resistance of sintered and sprayed LSGM, respectively. However, the low-frequency intersection is different between sprayed and sintered LSGM. This reflects in principle the difference in Pt/LSGM interface between the plasma sprayed sample and conventionally pressed sample.

![Figure 5-15 Comparison of ac complex impedance between sprayed and sintered LSGM at 800°C](image)

5.4 Summary

Exercise of plasma spraying LSGM electrolyte layers on SWPC’s cathode substrates has been performed under this add-on task. The results clearly demonstrated the technical feasibility of successfully plasma-spraying LSGM thin-films. Due to the unique physicochemical properties owned by LSGM material, plasma spraying LSGM does not require high level of power. The as-sprayed LSGM tends to be amorphous and needs post-spray annealing above 800°C to become crystallized. Additional attention is also needed to consider potential material loss during plasma spray so that a certain compensation can be implemented. Failure to do so would result in formation of secondary phases in LSGM. With a right initial chemistry of LSGM and plasma spray parameters, fabrication of high quality LSGM film on SWPC’s cathode substrate is achievable at much lowered post-spray heat treatment temperature.
REFERENCES