Synthesis and Characterization of La, Sc, Yb and Nd co-doped Gadolinium doped Cerium (GDC) Composite Electrolyte for IT-SOFC

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Abstract. Composite based on gadolinium doped cerium (GDC) co-doped Lanthanum (La), Scandium (Sc), Ytterbium (Yb) were investigated as electrolyte for solid oxide fuel cell (SOFC), namely GDC-La, GDC-Sc, GDC-Yb and GDC-Nd, respectively. The second co-doped La, Sc, Yb and Nd ensured the stability and high ionic conductivity of the GDC ceria-based electrolyte materials for SOFC. The GDC powder was synthesized via sol-gel technique. Then the La-GDC, Sc-GDC, Yb-GDC and GDC-Nd were subsequently prepared by mixing the GDC with La, Sc, Yb, and Nd respectively, through solid-state reaction in ballmill at 200rpm alumina balls. The composite electrolytes were then characterized in terms of its morphology, phase and thermal properties of the powders. Among the composite electrolytes investigated, GDC-Yb powder show higher purity and better dispersion than the others co-doped GDC. TGA analysis present that the addition of co-dopant led to improve thermal resistance and stability of solid electrolyte powders. The results confirm that GDC with co-dopant is promising alternative electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFC).

1. Introduction
Fuel cells are electrochemical device that directly convert chemical energy from a fuel into electricity. This device produces electricity with no harmful byproduct for environment [1]. When hydrogen rich fuel such as natural gas passes through fuel cells, it electrochemically reacts with the oxygen to produce electricity, heat and water. These results in power generation that is essentially no present of nitrogen oxide (NOx), sulfur dioxide (SOx) or particulate matter that assists in reduction of air pollution and hazardous gas emission. Fuel cells are classified based on type of electrolyte used namely alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), proton exchange membrane fuel cell (PEMFC), and solid oxide fuel cell (SOFC). Among the various types of fuel cells, solid oxide fuel cell has been widely developed and its technology has been extensively adopted.

Solid oxide fuel cell technology is promising system for generating electricity due to its high conversion efficiency from chemical energy into electricity [2]. SOFC has many advantages over another type of fuel cells. First, due to its high operating temperature, no precious metals are required as catalyst. It potentially reduces the cost for its manufacturing. Second, SOFC has high resistance to sulfur gas. It is more flexible to various kinds of fuel where it can internally reform methane gas so
that no reformer is needed. Third, SOFC is not experiencing carbon monoxide gas poisoning; even it can be used as fuel and this advantage makes SOFC can utilize gas from coal.

SOFC operates at high temperature and it causes instability for the system for long term period, high manufacturing cost and difficulties in selection of appropriate materials. Recently, the further research has been conducted on SOFC system which operates at medium temperature (600-800°C) [3]. Lowering of operating temperature in SOFC has been attracted much attention of some researchers due to it gives some advantages such as employing cheaper materials but still have good performance, high stability of electrolyte and rapid start up process [4].

Ceria-based electrolyte has received much more attention and considered as the best material for intermediate SOFC [5]. Aliovalent dopants such as Yb₂O₃, Gd₂O₃, La₂O₃ and Sc₂O₃ will react with CeO₂ and establish vacancies in crystal lattice as of facilitate oxygen ion to move. Accordingly, the ion of dopants will easily make a bonding with Ce³⁺. Ion vacancies has important role towards ionic conductivity in ceria-based electrolyte [6]. Gadolinium doped cerium (GDC) is considered as one of the best choice among ceria-based electrolytes [7].

Strategy of co-dopant addition in solid electrolyte shows better conductivity than single-doped. Co-doped electrolyte materials might sort the oxygen vacancy become more organized so as ease of oxygen ion stepping and increase ionic conductivity. For example, N. Kim et al [8] reported the addition of five trivalent metal (Y, Sm, Nd, Pr and La) oxide as co-dopant materials for 20 mol% of GDC results indicated that the addition of co-dopant in GDC solid electrolyte can generally improve its electrical properties. It is also reported by Maricle et al [9] that electrolyte domain regime increased by two order of oxygen partial pressure through the addition of 3 mol% Pr into GDC. Although co-dopant addition into GDC has been studied by several researchers, it is still somewhat unclear how co-dopant addition affects the properties of SOFC electrolyte.

Co-doping approach with two or more aliovalent was known improving conductivity over single doping [10]. Based on this, in present work was focused on addition of co-dopant in GDC synthesis for solid electrolyte for SOFC. Oxides metal of La₂O₃, Sc₂O₃ and Yb₂O₃ were used as second dopant for GDC. The GDC powder was synthesized via sol-gel method and the dopant was added through solid state reaction in ballmill. The properties of co-doped GDC were then characterized in term of its morphology, compositional properties and thermal properties of the powders.

2. Experimental

First, gadolinium doped cerium powders with composition of Gd₀.₉₀Ce₀.₀₉O₁₀ (GDC10) were synthesized by using sol-gel method. Cerium nitrate hexahydrate and gadolinium nitrate hexahydrate were used as starting materials. While as solvent and metal chelating agent, it was used demineralized water and citric acid monohydrous respectively. At the beginning, starting materials was mixed in the required stoichiometric ratio after each homogeneously dissolved. Citric acid was added into the mixture of precursors to maintain the total molar ratio of metal to citric acid. The solution was stirred and then temperature was raised to 80°C. Stirring was still maintained around 1 hour until it turned into yellow color and foam was formed. Sample was kept at room temperature and then it was dried in an oven at temperature of 110°C for about 24 hours. After drying, sample was grinded by using mortar grinder into the fine powders and then it was calcined at temperature of 700°C.

Second, metal oxides consisting of La₂O₃, Sc₂O₃ and Yb₂O₃ as co-dopants were added into successfully synthesized GDC10 through solid state reaction. The co-dopant addition was amount of 1%wt of GDC using ball mill. The weighed powders were mixed in ball mill jar and ethanol was added as dispersant to maintain colloid system in the mixture. Aluminum balls were used as mixing media in the ball mill. Speed rotation was 240 rpm for approximately 4 hours with 30 minutes of resting time. After co-doping step, sample powders were dried at temperature of 110°C for 24 hours in an oven.

The co-doped GDC powders were then characterized using Scanning Electron Microscope (HITACHI SU3500, Japan) to and Energy Dispersive X-Ray (EDX) to analyze structural and compositional properties, respectively. Thermal Gravimetric Analysis (LabSys Evo TG-DTA, France)
was performed to investigate thermal properties of samples. In addition, ionic conductivity of selected sample was also measured.

3. Results and Discussion

Figure 1 shows SEM images of co-doped GDC powders of all samples after calcined at temperature of 700°C. It can be seen that the powders appearance looks like flakey shape at most and some of them at small amount shows to have porous nature if observed at higher magnification.

![SEM images of co-doped GDC powders](image)

**Figure 1.** SEM image of co-doped GDC powders (a) GDC-La; (b) GDC-Sc; (c) GDC-Yb; and (d) GDC-Nd after calcined at temperature of 700°C

Figure 2 shows EDX spectrum results of GDC-La sample consisting of lanthanum, gadolinium and cerium element. The composition of lanthanum as second dopant or co-dopant is much smaller than gadolinium as main dopant, as expected. From EDX quantitative analysis of elements, lanthanum content on the sample powders in spectrum 3 was about 0.41wt% and 0.13at% as shown in Table 1. While gadolinium as first dopant was detected as much as 7.39wt% and 2.01at%. Another EDX spectrum shows almost similar results of quantitative element analysis. However, lanthanum was not found in all of EDX spectrums but only in spectrum 3, suggesting that co-dopant was still not homogeneously dispersed. Moreover, in this GDC-La sample powders, it was found peak indicating aluminum impurity that might come from alumina ball used as mixing media in ball milling process. These results suggested that the preparation of co-doped GDC powders need to be carefully performed
in order to obtain homogeneous dispersion of co-dopant with no impurities. N. Kim et al. [8] has prepared co-doped GDC powders with no impurities by using Pechini process including incorporation of selected five trivalent metal (Y, Sm, Nd, Pr and La) as co-dopant. Meanwhile, in this work, co-dopant was added by solid state method through ball milling process.

![Figure 2. (a) EDX point analysis of GDC-La sample (b) EDX results of spectrum 3](image)

Similar with GDC-La, in GDC-Sc and GDC-Nd sample powders were also found that the co-dopant dispersion was not sufficiently uniform. It can be seen from EDX elemental analysis that showing not all of point spectrum consisted of co-dopant element of Sc and Nd, respectively.

| Element | Weight% | Atomic% |
|---------|---------|---------|
| O K     | 29.41   | 78.68   |
| La L    | 0.41    | 0.13    |
| Ce L    | 62.79   | 19.18   |
| Gd L    | 7.39    | 2.01    |
| Totals  | 100.00  |         |

In case of ytterbium element addition into GDC namely GDC-Yb, the dispersion of co-dopant seems relatively more uniform in the powders. It can be seen from EDX element analysis which was identifying peak spectrum of Yb in every investigated point.

The present of Yb co-dopant was confirmed by EDX analysis with the concentration of 0.71wt% and 0.16at% in point of spectrum 4 like shown in Table 2. The concentration of gadolinium element was in the amount of 7.44wt% and 1.83at%. Another points exhibited identical results of EDX elemental analysis. There is also no other impurities found in this GDC-Yb sample powders, but only gadolinium, cerium and ytterbium present. The purity of GDC-Yb powders seems to be higher than the others co-doped GDC.
Figure 3. (a) EDX point analysis of GDC-Yb sample (b) EDX results of spectrum 1

Table 2. EDX quantitative analysis of spectrum 4 from GDC-Yb sample

| Element | Weight% | Atomic% |
|---------|---------|---------|
| O K     | 33.99   | 82.06   |
| Ce L    | 57.87   | 15.95   |
| Gd L    | 7.44    | 1.83    |
| Yb L    | 0.71    | 0.16    |
| **Totals** | **100.00** |         |

Figure 4 shows TGA plot for un-doped GDC and co-doped GDC at intermediate operating temperature of SOFC. From the results, it is found that there is no weight loss observed at those range of temperature. The graph is relatively flat indicating that no decomposition occurred. From the point of view of Intermediate Temperature SOFC (IT-SOFC) which operate at temperature of 600-800°C, this materials are regarding as promising solid electrolyte for SOFC [4]. It is comparably stable in which to address the challenge of degradation problem in SOFC technology. However, thermal stability is becoming the main issue when the device is subjected to high temperature operation.

It can be observed also that GDC with co-dopants addition presenting slightly higher level of TG% compared with un-doped GDC. It indicates that the addition of co-dopant led to improve thermal resistance and stability of solid electrolyte. From the graph in Figure 4, we can see also that GDC-Yb has slightly lower TG% compared with other co-doped GDC. According to N. Kim et al. [8], thermal properties that were represented by thermal expansion coefficient (TEC) value slightly changed around 5% with the addition of co-dopant. The change in TEC might be related with the change of lattice parameter. They also reported that co-dopants addition (Y, Sm, Nd, La) slightly changed the value of TEC, except the addition of Pr co-dopant which TEC rapidly increased.
Figure 4. Thermal Gravimetric Analysis (TGA) plot of un-doped GDC and co-doped GDC at range of intermediate operating temperature of SOFC

The powders were pressed into a pellet and sintered at temperature of 1050°C and 1150°C. Then, it was performed ionic conductivity measurement where in this case, only GDC-Nd was selected. Figure 5 shows ionic conductivity of selected sample of GDC-Nd at different operating temperature and activation energy values of a certain temperature range. Total conductivity increase as temperature increase. The highest total ionic conductivity for GDC-Nd sample was about 0.040 Scm⁻¹ at 800°C for GDC-Nd sintered at 1150°C, as shown in Table 3. While for GDC-Nd sample sintered at temperature of 1050°C shows highest total ionic conductivity of 0.026 Scm⁻¹. It implies that higher sintering temperature gives higher ionic conductivity where higher ionic conductivity could be related to the increase of number of equi-interaction energy site which reduces the activation energy and facilitates diffusion of ion oxygen in the crystal lattice [13]. It was reported by N. Kim et al [8] that electrical conductivity increased as much as 0.046 Scm⁻¹ with the addition of Nd (1 mol%) into GDC. This is in accordance with the results we obtained. However, sintering temperature in our work was about 1150°C while they sintered the electrolyte pellet disc at higher temperature of 1400°C.
Figure 5. Ionic conductivity of GDC-Nd pellet at two temperature sintering of 1150°C and 1050°C

Table 3. Total ionic conductivity for GDC-Nd electrolyte

| Sintering temperature | Total ionic conductivity, $\sigma$ (Sm$^{-1}$) |
|-----------------------|-----------------------------------------------|
|                       | 800°C | 750°C | 700°C | 650°C | 600°C | 550°C | 500°C |
| 1150°C                | 0.040 | 0.034 | 0.029 | 0.022 | 0.015 | 0.009 | 0.005 |
| 1050°C                | 0.026 | 0.024 | 0.019 | 0.017 | 0.009 | 0.006 | 0.003 |

4. Conclusion
Composite based on gadolinium doped cerium (GDC) co-doped lanthanum (La), scandium (Sc), ytterbium (Yb) and neodymium (Nd) were investigated as electrolyte for solid oxide fuel cell (SOFC), namely GDC-La, GDC-Sc, GDC-Yb and GDC-Nd respectively. GDC powders were successfully synthesized via sol-gel method and addition of metal oxide as co-dopant has been done with solid state reaction. SEM images show that the synthesized powders are sticking each other indicating particle agglomeration. The present of co-dopant on the powders were well confirmed by EDX analysis. GDC-Yb powders seem having higher purity than the others co-doped GDC and dispersed better. TGA analysis present that the addition of co-dopant led to improve thermal resistance and stability of solid electrolyte powders. The results confirm that GDC with co-dopant addition is a promising alternative electrolyte for intermediate temperature solid oxide fuel cells. Further investigations need to be performed later on.
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