



# Alkali resistant Ni-loaded yolk-shell catalysts for direct internal reforming in molten carbonate fuel cells



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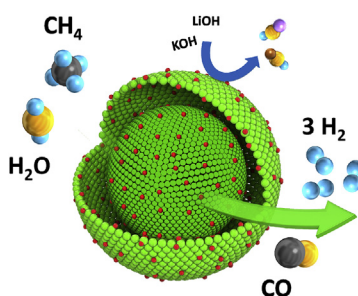
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## HIGHLIGHTS

- Ni yolk-shell catalysts are synthesized by a simple spray pyrolysis process.
- Ni yolk-shell catalysts on various supports are applied to DIR-MCFC.
- Ni@Al<sub>2</sub>O<sub>3</sub> shows the highest CH<sub>4</sub> conversion even on exposure to alkali hydroxide.
- Catalytic performance is strongly dependent on acidity and partly on reducibility.
- Acidic nature with yolk-shell structure enhances resistance to alkali poisoning.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A facile and scalable spray pyrolysis process is applied to synthesize multi-shelled Ni-loaded yolk-shell catalysts on various supports (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, and La(OH)<sub>3</sub>). The prepared catalysts are applied to direct internal reforming (DIR) in a molten carbonate fuel cell (MCFC). Even on exposure to alkali hydroxide vapors, the Ni-loaded yolk-shell catalysts remain highly active for DIR-MCFCs. The Ni@Al<sub>2</sub>O<sub>3</sub> microspheres show the highest conversion (92%) of CH<sub>4</sub> and the best stability among the prepared Ni-loaded yolk-shell catalysts. Although the initial CH<sub>4</sub> conversion of the Ni@ZrO<sub>2</sub> microspheres is higher than that of the Ni@CeO<sub>2</sub> microspheres, the Ni@CeO<sub>2</sub> microspheres are more stable. The catalytic performance is strongly dependent on the surface area and acidity and also partly dependent on the reducibility. The acidic nature of Al<sub>2</sub>O<sub>3</sub> combined with its high surface area and yolk-shell structure enhances the adsorption of CH<sub>4</sub> and resistance against alkali poisoning, resulting in efficient DIR-MCFC reactions.

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## 1. Introduction

A molten carbonate fuel cell (MCFC) is an ultraclean solution for stationary power generation [1,2]. In general, a temperature of ~650 °C is required to obtain sufficient conductivity of a carbonate electrolyte. Aside from electricity, heat is also produced by

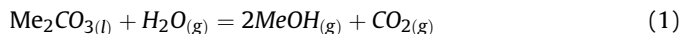
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electrochemical reactions. Therefore, by combining an electrochemical cell producing heat with a reforming reactor, direct internal reforming (DIR) is possible, where DIR directly utilizes the heat and steam produced by electrochemical reactions [3–5]. In addition, the conversion of CH<sub>4</sub> is promoted by the reduction of the H<sub>2</sub> partial pressure, which is caused by the consumption of H<sub>2</sub> in electrochemical reactions. Thus, DIR has advantages regarding the overall efficiency and CH<sub>4</sub> conversion. However, a significant challenge for DIR-MCFCs is deactivating the steam methane reforming (SMR) (CH<sub>4</sub> + H<sub>2</sub>O ↔ CO + 3H<sub>2</sub>) catalyst that occurs when the catalyst is in contact with alkali metals [6–8]. The presence of steam transforms the molten carbonate electrolytes into alkali hydroxide vapors, thereby depositing them onto the DIR catalysts.



The deposition of alkali metals onto the DIR catalysts causes catalyst deactivation in several different ways, including the formation of a less active (111) plane, sintering of Ni or the support, and blockage of external or internal active surfaces [6–9]. Therefore, it is necessary to develop alkali-resistant catalysts for DIR-MCFCs.

Core/yolk-shell catalysts have attracted special interest in the field of energy-related applications, such as hydrocarbon reforming reactions and high-temperature fuel cells [10]. Kawi's group has explored the enhanced performance of yolk-shell catalysts in the dry reforming of methane [11,12]. They studied the effect of the treatment duration and shell thickness on yolk-satellite-shell structured Ni-yolk@Ni@SiO<sub>2</sub> catalysts and found that the formation of small satellite Ni particles and yolk-shell structures contributed to their high catalytic activity and stability [12]. Zhang's group investigated core-shell Ni@SiO<sub>2</sub> catalysts for use in DIR-MCFCs and demonstrated that the shell acted as a transport barrier against alkali hydroxide vapor, protecting Ni particles from alkali poisoning [13,14]. Many studies have reported that core/yolk-shell catalysts have enhanced catalytic stability [10,15]. In particular, their structure is effective at protecting active sites against poisoning and inhibiting sintering of active metals or supports [16–18]. Recently, Kang's group successfully synthesized multi-shelled yolk-shell microspheres with various compositions using an easy and scalable spray process [19–23]. The synthesized yolk-shell microspheres have excellent characteristics for use as electrodes in rechargeable batteries and gas sensors. The spray process has unique advantages for large-scale production of yolk-shell microspheres, allowing the formation of microspheres with complex compositions and uniform distributions of active materials without the need for expensive templates. However, yolk-shell microspheres prepared by spray processes have not been applied as catalysts for chemical conversion reactions. In particular, non-precious metal loaded yolk-shell microspheres produced by the spray process have not been studied. Ni has typically been used as a non-precious active metal for reforming reactions [24]. Several supports have been studied to enhance their catalytic performance and resistance against alkali poisoning [25–28]. Al<sub>2</sub>O<sub>3</sub> exhibited strong bonding with alkali metals [25]. CeO<sub>2</sub> showed unique redox properties resulting from the mobility of the oxygen in its lattice [26,27]. ZrO<sub>2</sub> is well-known to be a highly stable material at high temperatures and La<sub>2</sub>O<sub>3</sub> was reported to improve the dispersion of active metals [26,28].

In this study, Ni-loaded yolk-shell catalysts were prepared by a facile, scalable spray pyrolysis process and applied to a DIR-MCFC. The influences of various support materials (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, and La(OH)<sub>3</sub>) on the catalytic performance for the DIR-MCFC reaction were systematically investigated. The physicochemical properties of the prepared catalysts were evaluated to correlate

their reforming activity and resistance against alkali poisoning.

## 2. Experimental

### 2.1. Catalyst preparation

Ni-loaded yolk-shell microspheres (15 wt% Ni@CeO<sub>2</sub>, Ni@ZrO<sub>2</sub>, and Ni@La(OH)<sub>3</sub>) were prepared by spray pyrolysis and a subsequent reduction process. NiO-loaded yolk-shell microspheres of Ni@CeO<sub>2</sub>, Ni@ZrO<sub>2</sub>, and Ni@La(OH)<sub>3</sub> were prepared by a one-pot spray pyrolysis process from a spray solution containing sucrose, Ni salts, and a supporting material. NiAl<sub>2</sub>O<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> yolk-shell microspheres were prepared by a spray pyrolysis process and a subsequent post-treatment in an air atmosphere at 900 °C. The reduction of the NiO catalyst was carried out at 650 °C for 2 h before the reaction to form Ni-loaded yolk-shell microspheres. The spray pyrolysis system applied in this study is shown in Fig. S1. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate many droplets. A quartz reactor, 1200 mm in length and 50 mm in diameter, was used at an air gas flow rate (carrier gas) of 5 L min<sup>-1</sup>. The reactor temperature during the spray pyrolysis process was fixed at 900 °C. Aluminum nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Junsei, Japan), lanthanum nitrate hexahydrate (La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, GFS Chemicals, Italy), cerium (III) nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Samchun, Korea), zirconyl nitrate hydrate (ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O, Sigma-Aldrich, USA), and nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Samchun, Korea) were used as the source materials for the Ni, Al, La, Ce, and Zr components, respectively. For the Ni@Al<sub>2</sub>O<sub>3</sub> catalyst, the concentrations of aluminum nitrate and nickel nitrate dissolved in distilled water were 0.2 M and 15 wt%, respectively. The concentration of sucrose used as the carbon source material to form the yolk-shell structure in the spray pyrolysis process was fixed at 0.5 M.

### 2.2. Characterization

The crystal structures and morphologies of the Ni-loaded yolk-shell microspheres were investigated using XRD (Rigaku DMAX-33) at the Korea Basic Science Institute (Daegu), SEM (TESCAN VEGA3-SB), and HR-TEM (JEOL, JEM-2100F). The BET surface areas of the catalysts were determined by N<sub>2</sub> physisorption at 77 K using an accelerated surface area and porosimetry system (ASAP 2010, Micromeritics). Before analysis, samples were degassed for 12 h at 110 °C under vacuum, at a pressure of less than 0.5 mm Hg. H<sub>2</sub> chemisorption was performed in an Autochem 2920 (Micromeritics). The catalyst was reduced at 650 °C for 2 h in a 10% H<sub>2</sub>/Ar flow. After adjusting the temperature of the catalyst bed to 50 °C, H<sub>2</sub> was added to the catalysts until H<sub>2</sub> saturation occurred. From the amount of chemisorbed H<sub>2</sub>, the Ni dispersion was calculated, assuming that the adsorption stoichiometry was one hydrogen atom for one surface Ni atom (H/Ni<sub>surface</sub> = 1). X-ray photoelectron spectroscopy (XPS) analysis was conducted using an AXIS-NOVA spectrometer (Kratos Analytical Ltd.). XPS spectra were recorded using Al K<sub>α</sub> monochromatic (1486.6 eV) X-rays. A pass energy of 160 eV was used for the survey scan and 40 eV for the narrow scan. All binding energies were adjusted to the C1s peaks at 284.6 eV. XANES was performed at the 8C Nano XAFS beamline of the Pohang Accelerator Laboratory, Republic of Korea. H<sub>2</sub>-TPR experiments were carried out in an Autochem 2920 (Micromeritics). Typically, 0.1 g of sample was loaded into a quartz reactor. H<sub>2</sub>-TPR measurements were performed using 10% H<sub>2</sub>/Ar gas at a heating rate of 10 °C min<sup>-1</sup>. NH<sub>3</sub>-TPD experiments were performed on an Autochem 2920 (Micromeritics). Samples (0.3 g) in a quartz reactor were pretreated with He gas at 800 °C for 1 h and then cooled. NH<sub>3</sub> was adsorbed at 100 °C for 30 min, and weakly adsorbed CO<sub>2</sub> was

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