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## Stability of lithium aluminate in reducing and oxidizing atmospheres at 700 °C

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### ABSTRACT

The stability of lithium aluminate ( $\text{LiAlO}_2$ ) powders have been studied under reducing (4%  $\text{H}_2\text{-N}_2$ ) and oxidizing (Air) atmospheres at 700 °C. While XRD results show the raw  $\alpha\text{-LiAlO}_2$  samples contain a minor fraction of  $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$  and  $\text{LiAlO}_2 \cdot 0.25\text{H}_2\text{O}$  phases, high-temperature XRD study shows that  $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$  may have decomposed at 700 °C to  $\gamma\text{-LiAlO}_2$  and  $\text{LiAlO}_2 \cdot 0.25\text{H}_2\text{O}$  to  $\alpha\text{-LiAlO}_2$ . Surface morphological studies show the samples consist of porous  $\text{LiAlO}_2$  spherical agglomerates with interconnected nanoparticles. The XPS analyses indicate that the powder surface Li/Al ratio decreases after exposure to reducing atmosphere whereas much less change to the oxidizing atmosphere. The binding energy of Al 2p peak also changes in the high-temperature reducing and oxidizing environments, indicating the presence and co-existence of different oxidation states of Al species on the surface. The color of  $\text{LiAlO}_2$  powder, examined visually, changed from white to gray after reduction and back to white after re-oxidation, indicating the likelihood of generation of non-stoichiometry under reducing atmosphere.

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### Introduction

Lithium aluminate ( $\text{LiAlO}_2$ ) has been extensively used for over three decades as a ceramic constituent material of the electrolyte matrix structure in molten carbonate fuel cell (MCFC) stacks for stationary power generation [1,2]. MCFCs operate at intermediate temperatures in the range of 550–650 °C and offer high electrical and combined heat and power (CHP) efficiency (>47% single-cycle electrical and >85% CHP). A wide variety of fuels derived from renewable resources (bio-fuels) and fossil fuels (coal and natural gas) have been successfully

utilized in MCFCs. Although 40,000–50,000 h of operation has been demonstrated at MW class MCFCs, further enhancements in operating life time and cell performance stability are considered important for accelerating large scale commercialization and global market penetration. The porous electrolyte matrix, which acts as an electrolyte retainer, has been considered as one of the most critical stack component impacting cell life and performance; continuous particle coarsening and structural changes could result in reduced capability of electrolyte retention, faster electrolyte loss and increased gas crossover [3].  $\text{LiAlO}_2$  exists in three different

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allotropic forms: the hexagonal  $\alpha$ -LiAlO<sub>2</sub>, tetragonal  $\gamma$ -LiAlO<sub>2</sub> and monoclinic  $\beta$ -LiAlO<sub>2</sub> [4] of which the  $\gamma$ -LiAlO<sub>2</sub> is the stable phase at higher temperatures, while  $\alpha$ - and  $\beta$ -LiAlO<sub>2</sub> phases show transformation to the  $\gamma$ -LiAlO<sub>2</sub> at elevated temperatures [5,6]. For example, at very-high temperatures (e.g., 937 °C),  $\alpha$ -LiAlO<sub>2</sub> can transform to  $\gamma$ -LiAlO<sub>2</sub> in air after 40 h [7]. Particle coarsening and phase transformation of LiAlO<sub>2</sub> have been reported as one important cause for in-cell electrolyte depletion in MCFC [8]. Although  $\gamma$ -LiAlO<sub>2</sub> has initially been considered stable in MCFC, its instability has been revealed to result in the accelerated electrolyte loss and cell failure in long-term cell operation [9]. Since mid-1990s  $\alpha$ -LiAlO<sub>2</sub> has been recognized as a more stable matrix support material for current commercial MCFC deployment [10]. Nevertheless, fundamental understandings of its stability still need to be investigated for helping designing approaches to achieve durability for  $\geq 10$ -year service life.

LiAlO<sub>2</sub> has also found application as a solid tritium breeding material in nuclear fusion reactors due to its excellent thermochemical and mechanical stability at high temperature and favorable irradiation behavior [1,2]. Apart from application in nuclear systems, LiAlO<sub>2</sub> has also found application as an excellent luminescent material [11].  $\gamma$ -LiAlO<sub>2</sub> provides an attractive red phosphor for artificial illuminations [12].

A number of synthesis processes including conventional solid-state reactions, sol–gel processing, co-precipitation and combustion synthesis have been extensively used for the preparation of LiAlO<sub>2</sub> powder. Solid-state synthesis in the range of 370 °C–1000 °C has been reported to lead to the formation of a mixture of LiOH and a lithium dialuminate, depending on the calcination temperature [13,14]. The process was found difficult for the synthesis of pure lithium aluminate with controlled size and morphology due to partial evaporation of lithium at higher temperatures and contamination from grinding operations [15].  $\alpha$ -LiAlO<sub>2</sub> has been synthesized using oxide and salt precursors. A mixture of Li<sub>2</sub>CO<sub>3</sub> and Al(OH)<sub>3</sub> were dried at 60 °C for 24 h followed by heat-treated at 650 °C for 24 h in a pure CO<sub>2</sub> atmosphere. The final powders were produced by eliminating the residual carbonate by washing [16]. Formation of minor-phase lithium aluminum oxide hydrate, LiOH·2Al(OH)<sub>3</sub>·2H<sub>2</sub>O (or LiAl<sub>2</sub>(OH)<sub>7</sub>·2H<sub>2</sub>O) during powder synthesis was found to transform easily to  $\gamma$ -

LiAlO<sub>2</sub> during exposure to nitrogen atmosphere at elevated temperatures [17].

Sol–gel technique has been used for preparing  $\gamma$ -LiAlO<sub>2</sub> utilizing the hydrolysis of lithium and aluminum alkoxide followed by calcination at temperature of 550 °C [17]. The technique showed the limitation in terms of instability of precursors, precise control of reaction steps and use of expensive reactants. Use of co-precipitation technique provided pure  $\gamma$ -LiAlO<sub>2</sub> in the presence of nonionic surfactant after calcination at 950 °C [15]. The combustion synthesis technique using glycine nitrate–urea reactants was also found suitable for synthesizing  $\gamma$ -LiAlO<sub>2</sub> [18,19].

As mentioned earlier, sufficient LiAlO<sub>2</sub> stability under MCFC operating environment is essential to assure long-term electrolyte retention for stable cell resistance and performance. LiAlO<sub>2</sub> in matrix experiences both reducing anode and oxidizing cathode atmospheres. However, detailed LiAlO<sub>2</sub> structure thermal stability under various gas atmospheres have been reported in the literature only to a limited extent. Discoloration of  $\gamma$ -LiAlO<sub>2</sub> powders have been reported due to the presence of residual amorphous carbon-containing compounds resulting from incomplete oxidation of the glycine-urea by the combustion synthesis technique [20]. Color change from white to dark blue in oxides such as Li<sub>2</sub>TiO<sub>3</sub> exposed to reducing conditions has been attributed to oxygen non-stoichiometry and formation of vacancies and compound such as Li<sub>2-x</sub>TiO<sub>3-y</sub> [21].

In the present paper, we have investigated the structural and chemical stability of  $\alpha$ -LiAlO<sub>2</sub> under reducing and oxidizing atmospheres at 700 °C. We further develop fundamental understandings of the effect of crystalline structure, surface composition, and morphology on thermal stability.

## Experimental

### Materials and methods

The LiAlO<sub>2</sub> powder samples were prepared by solid-state synthesis method reported by Choi et al. [16]. The precursor materials, Al(OH)<sub>3</sub> (>99.9% pure) and Li<sub>2</sub>CO<sub>3</sub> (>99.9% pure), were mixed with deionized water in the different molar ratio to control Li/Al ratio by ball milling. Uniformly dispersed

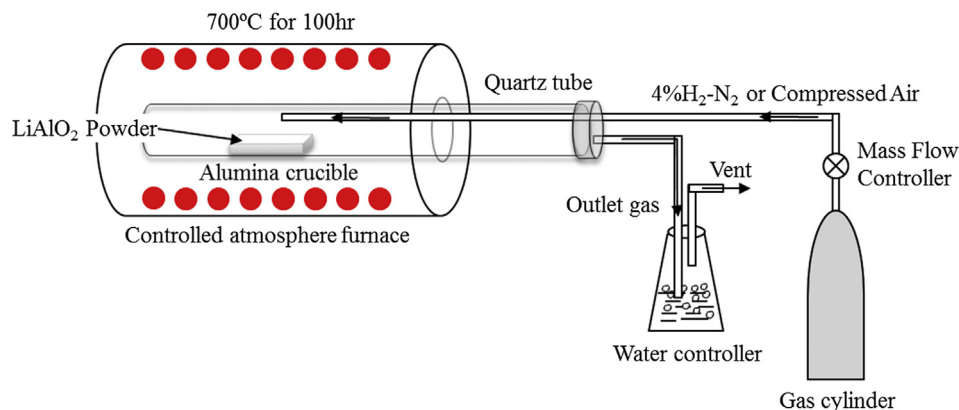


Fig. 1 – Schematic setup for controlled reduction and oxidation of LiAlO<sub>2</sub>.

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