

## Synthesis and characterization of solid electrolyte structure material ( $\text{LiAlO}_2$ ) using different kinds of lithium and aluminum compounds for molten carbonate fuel cells

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Synthesis and characterization of solid electrolyte structure material using different kinds of lithium and aluminum compounds for molten carbonate fuel cells have been carried out. Synthesis operations are performed using three different kinds of lithium compounds ( $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{LiNO}_3$  and  $\text{Li}_2\text{CO}_3$ ) and two different kinds of aluminium compounds ( $\text{Al}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$ ). During the synthesis, all the reactions are conducted at four different pH levels (1.5, 4, 9.5 and 12) and are calcinated at three different temperatures in open air conditions. In the light of thermal, structural and surface area characterization (TG-DTA, XRD and BET analyses), it is concluded that  $\text{LiAlO}_2$  which is produced with  $\text{Li}_2\text{CO}_3$  and  $\text{Al}(\text{OH})_3$ , is found to be convenient.

**Keywords:** Electrolyte, Molten carbonate fuel Cell,  $\text{LiAlO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$

Molten carbonate fuel cells (MCFC), which are proposed to be used generally in stationary energy production systems and are likely to replace the thermal plants, are one of the best among clean energy production systems aiming at electricity generation. They operate at medium temperature (650-680°C) and their power generation yield is better than the traditional systems.

The state of the art MCFC consists of a porous nickel anode which contains dispersed aluminum or chromium to provide strength and sintering resistance, a porous, lithium-doped, nickel oxide cathode, and a lithium aluminate matrix filled with lithium and potassium carbonates as the electrolyte. The increase of cell life is one of the most important targets for MCFC to be brought into actual application. A key point in the development of electrode materials for MCFCs is the improvement in their chemical and physicochemical stability<sup>2</sup>.

In MCFC technology, the electrolyte, that is the ion conductor, is a mix of alkaline salts, molten at the operating temperatures and held in a ceramic porous support called matrix. This is one of the most critical components because it allows the ionic conductivity between anode and cathode, acting at the same time

as both a gas barrier and an electronic insulation layer between the two parts of the cell. For this purpose, the matrix must have a retention capacity, which is controlled by its porosimetric structure<sup>3</sup>.

Basically the operation temperature of the electrolytic matrix consisting of electrolyte and the support unit carrying the electrolyte and  $\text{LiAlO}_2$  that has a task to direct the ions is approximately 650°C. One of the most important problems faced with molten carbonate fuel cells during their long-term operation at this high temperature is the structural degradation of electrolyte matrix resulting from the working temperature. As a result of this degradation, electrolyte matrix may cause leakages and short circuit. Research studies showed that lithium aluminates are a suitable one to be used as the main compound of this structure.  $\gamma$ - $\text{LiAlO}_2$  powders are the most commonly used materials in matrix production in molten carbonate fuel cells because it has a large specific surface area and modify the conductivity of electrolytes. However, the fact that the matrix limits its stability during long term operation is seen as the disadvantage of these materials. Therefore, in search of compounds without this disadvantage, several materials have been studied and the

investigation of properties of  $\alpha$ -LiAlO<sub>2</sub>, which is an allotrope of  $\gamma$ -LiAlO<sub>2</sub>, has gained considerable attention in recent years<sup>4-7</sup>.

In this study, to find suitable synthesis condition of LiAlO<sub>2</sub> material, which is a key component in the electrolyte matrix, was used at different Al and Li precursors under different pH and calcinations temperature. The measurement of some characteristic properties of synthesized LiAlO<sub>2</sub> was investigated. The LiAlO<sub>2</sub> is then transformed from powder form to plates with help of organic binders. The generation of matrix by drying and calcinations and some characteristics properties were also investigated.

### Experimental Section

Experimental studies were carried out in three steps: the synthesis of LiAlO<sub>2</sub> material, the production of green sheets and the measurement of some characteristic properties of synthesized LiAlO<sub>2</sub> samples. In the synthesis of LiAlO<sub>2</sub>, three lithium compounds (LiOH.H<sub>2</sub>O, LiNO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>) were used as lithium source and Al<sub>2</sub>O<sub>3</sub> and Al(OH)<sub>3</sub> compounds were used as aluminum source.

#### LiAlO<sub>2</sub> synthesis

In the synthesis prepared by using sol-gel technique, four different synthesis reactions were realized as shown in Equations 1, 2, 3, 4 by using five different compounds. Each synthesis was conducted at a temperature of 90°C and at four different pH levels (1.5, 4, 9.5 and 12) and then the production was realized via calcinations at high temperatures. The calcinations at high temperatures were performed at dry air medium and at three different temperatures (650, 800, 950°C) in periods of twenty four hours.



The purpose in each reaction was to produce 45 g LiAlO<sub>2</sub>, and the amounts of necessary reactants were calculated stoichiometrically and the first step of the synthesis process was completed by mixing the reactants in a magnetic agitated heater for 24 h at 90°C. The same procedures were repeated for each reaction at four different pH values (1.5, 4, 9.5 and 12). In these experiments, the precipitated LiAlO<sub>2</sub> was dried in the oven at 100°C and the compound formed was turned into the form of powder at the

mortar. Each sample was calcinated in the furnace at three different temperatures (650, 800, 950°C). The schematic illustration of the synthesis is given in Fig. 1.

#### Tape casting and matrix preparation

Electrolytic matrix was prepared by using tape casting method. In this method, LiAlO<sub>2</sub> particles in the form of powder were transformed into plates with the help of organic binders. During the experiments, poly-vinyl-butyril (PVB, Merck) was used as binding material. Absolute ethanol, poly-ethylene-glycol (PEG, Merck) and  $\alpha$ -terpineol (Merck) were used as solvent, plasticizer and dispenser, respectively. The PVB dissolved in the ethanol. After dissolving the PVB, PEG was added and mixed to form a uniform binder system. The ratio of PEG to PVB binder was about 0.5. Additionally,  $\alpha$ -terpineol (Merck) was added and stirred in a mixer for about 2 h to form a homogeneous slurry. The binder system and the synthesized LiAlO<sub>2</sub> powders were mixed and this was milled for 4 h in a 250 mL polypropylene jar with zirconia balls. Finally the slurry was casted on a smooth glass surface using a 6 inch-wide doctor blade. Pieces of the green tape were heated at various temperatures (650-950°C) for 4 h.

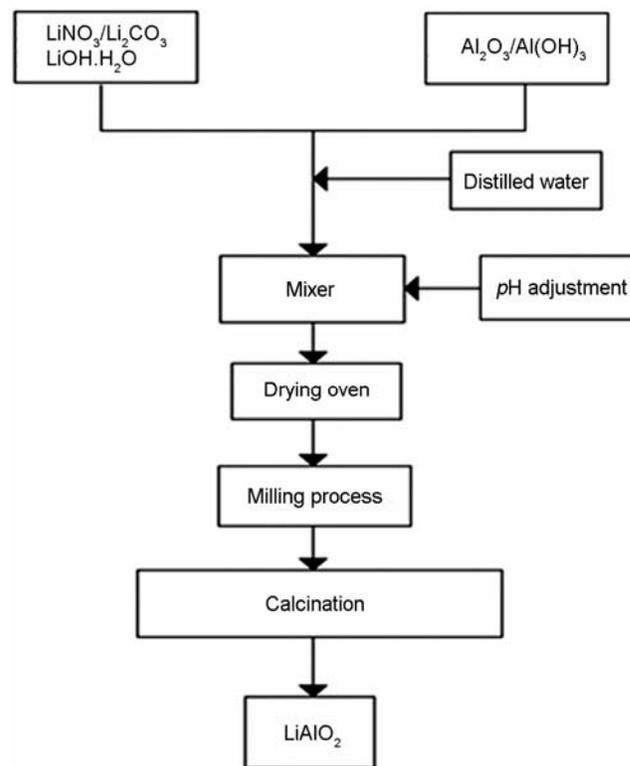


Fig. 1 — Schematic illustration of the synthesis of LiAlO<sub>2</sub> from lithium and aluminum sources

### Characterization studies

Phase of the samples was analyzed by X ray diffraction analysis (XRD: Model :Minflex X ray Diffractometer/PW 3710 Cu. $K\alpha_1$ ) at the step size of  $5^\circ < 2\theta < 80^\circ$  and the speed of  $1^\circ$ , Morphology and surface area of samples were examined by scanning electron microscope, (SEM: Model EOL), and particles size analyser BET (Quantochrome Nova 2200) respectively. Thermal behaviour of the samples was investigated using thermogravimetric analysis (TG) and differential scanning calorimeter (DSC) (Setrama brand 10011761 models TG-DTA machine).

### Results and Discussion

TG-DSC curve was plotted against temperature of the green tape prepared from  $\text{LiAlO}_2$  which is a result of  $\text{Li}_2\text{CO}_3 + \text{Al}(\text{OH})_3$  synthesis. It is seen that the first weight loss was at  $170\text{-}250^\circ\text{C}$ , the second important weight loss was at  $300\text{-}325^\circ\text{C}$ , and the last weight loss was at  $450\text{-}500^\circ\text{C}$ . Since the first one is an endothermic reaction, weight loss can be attributed to the removal of water in the system. The weight loss in the second part was explained as the degradation of some of the organic compounds used in tape production. Two exothermic reactions were observed between  $330\text{-}500^\circ\text{C}$ . The heat flux between  $330\text{-}400^\circ\text{C}$  was attributed to the burning of the organic structures, and the part between  $400\text{-}500^\circ\text{C}$  was explained as the completion of the  $\text{LiAlO}_2$  synthesis. It was also same from TG and DSC curves of green sheet which are a result of  $\text{LiOH}\cdot\text{H}_2\text{O} + \text{Al}(\text{OH})_3$ ,  $\text{LiNO}_3 + \text{Al}(\text{OH})_3$ ,  $\text{LiOH}\cdot\text{H}_2\text{O} + \text{Al}_2\text{O}_3$  synthesis. There was no difference between synthesized  $\text{LiAlO}_2$  and literature<sup>8</sup>. This is the expected result.

### Phase analysis

In order to determine the percentage of reactions and crystal structures of four samples synthesized  $\text{LiAlO}_2$ , X-ray diffractograms of the samples are given in Fig. 2. The data obtained from XRD graphs of  $\text{LiAlO}_2$  synthesized from  $\text{LiNO}_3 + \text{Al}(\text{OH})_3$  at  $950^\circ\text{C}$  were compared with index records of International Centre For Diffraction Data (card references of 73-1338) and it was determined that the data from the XRD belonged totally, 68%, to  $\gamma\text{-LiAlO}_2$ . In conclusion, a complete transformation was not achieved.

According to plots (a) and (c) in Fig. 3, it was 75%, to  $\gamma\text{-LiAlO}_2$  and 25% to cubic form  $\text{Li}_2\text{Al}_2\text{O}_4$  (card references of 01-1306), 60% to  $\text{Al}_2\text{O}_3$  and, 40% to  $\alpha\text{-LiAlO}_2$  (card references of 74-2232) respectively.

In conclusion, a complete transformation was not achieved. The data obtained from plot (b) were compared with index records (card references of 74-2232) and it was determined that the data from the XRD belonged totally, 100%, to  $\alpha\text{-LiAlO}_2$ . In conclusion, a complete transformation was achieved. Thus, it was suggested that  $\alpha\text{-LiAlO}_2$  should be an appropriate electrolyte support for a MCFC operating at around  $650^\circ\text{C}$ .

It was concluded that the synthesis of  $\text{LiAlO}_2$  from four Li and two different Al compounds at two different pH levels at three temperatures by using stoichiometric ratios was achieved with the highest efficiency and homogeneous crystalline structure from  $\text{Li}_2\text{CO}_3$  and  $\text{Al}(\text{OH})_3$  at  $\text{pH}=4$  at a low temperature. As for the other compounds, it was noted that the  $\text{LiAlO}_2$  formation could not be completed even at high temperatures.

### Electron microscope analysis

The analysis of Scanning Electron Microscope of green tape from  $\text{LiAlO}_2$ , a product of  $\text{Li}_2\text{CO}_3 + \text{Al}(\text{OH})_3$  synthesis, before and after calcinations were given in Fig. 3. According to the results obtained from Fig. 3a, the distance between the particles of  $\text{LiAlO}_2$  was determined as 2.5 and  $1.5\mu\text{m}$ . In Fig. 3b, it was determined as  $0.7\text{-}0.9\mu\text{m}$ . Here, it can be concluded that the pore size and consequently the porosity became smaller after the calcinations of the green tape. With this result, scientists working on porosity should take the required amount of  $\text{LiAlO}_2$  in the green tape for optimum efficiency into account.

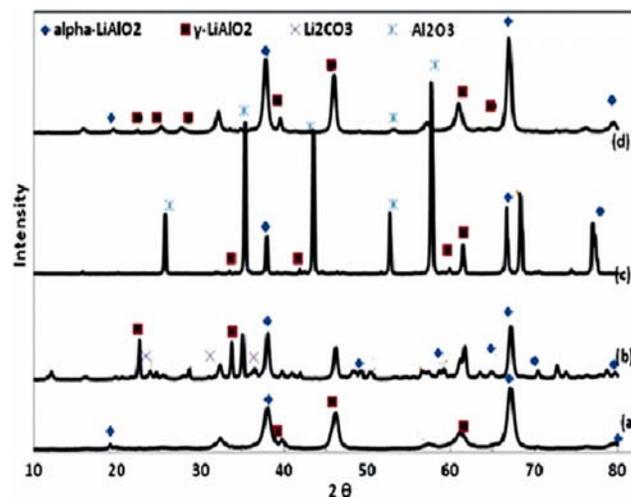


Fig. 2 — XRD graphs of  $\text{LiAlO}_2$  synthesized from a)  $\text{LiOH}\cdot\text{H}_2\text{O} + \text{Al}(\text{OH})_3$  at  $\text{pH}=4$  and  $T=950^\circ\text{C}$ ; b)  $\text{Li}_2\text{CO}_3 + 2\text{Al}(\text{OH})_3$  at  $\text{pH}=4$  and  $T=650^\circ\text{C}$ ; c)  $\text{LiOH}\cdot\text{H}_2\text{O} + \text{Al}_2\text{O}_3$ ,  $\text{pH}=12$  and at a temperature of  $800^\circ\text{C}$ ; d)  $\text{LiNO}_3 + \text{Al}(\text{OH})_3$ ,  $\text{pH}=12$  and  $T=950^\circ\text{C}$

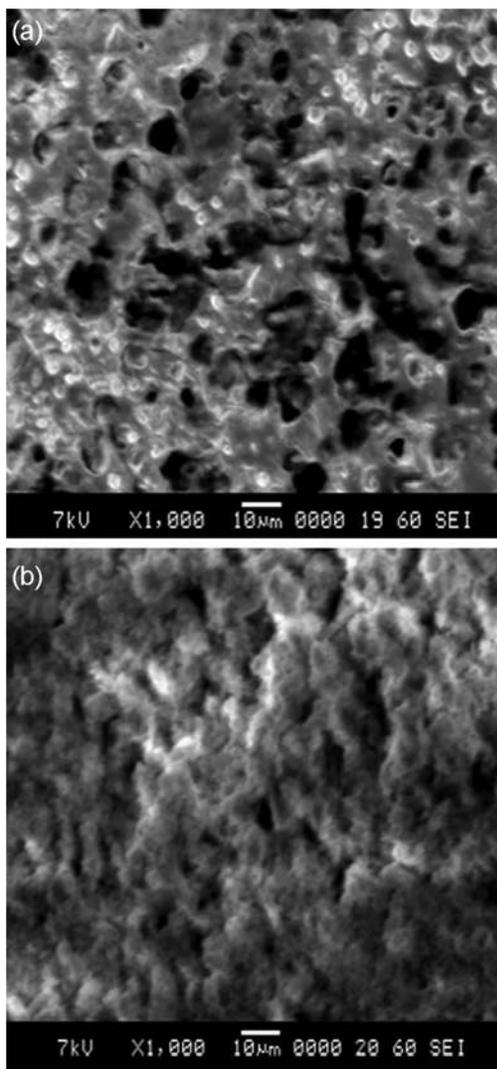


Fig. 3 — a) The SEM image of green tape before the calcinations; b) The SEM image of green tape after the calcinations (followed by 7 kV acceleration voltage and 1000 magnification)

#### Surface area analysis

A careful analysis of BET surface area measurements shows that  $\text{LiAlO}_2$  sample synthesized from  $\text{Li}_2\text{CO}_3 + \text{Al}(\text{OH})_3$  at  $\text{pH}$  9.5 and calcinated at  $650^\circ\text{C}$  had the maximum surface area of  $163.89 \text{ m}^2/\text{g}$  (Table 1). Also, Surface area measurement of commercial  $\text{LiAlO}_2$  was shown in Table 2.

In almost all calcinations experiments (Fig. 4), the surface area has decreased over  $650^\circ\text{C}$ , has reached to minimum around  $800^\circ\text{C}$  and has shown an increase around  $950^\circ\text{C}$ . Especially, the decrease around  $800^\circ\text{C}$  and increase again over this temperature has been attributed to the passing of  $\text{LiAlO}_2$  from  $\alpha$  phase to  $\gamma$  phase. It has also been attached to the increase in the micro pores in the

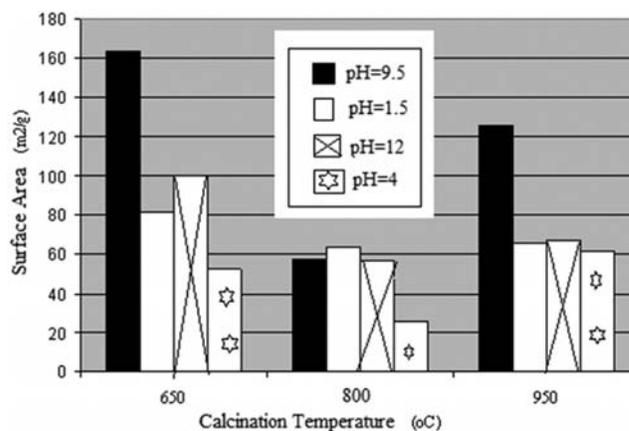


Fig. 4 — Surface areas of  $\text{LiAlO}_2$  synthesized at each calcinations temperature against  $\text{pH}$  values

Table 1 — Surface area measurements of  $\text{LiAlO}_2$  synthesized from  $\text{Li}_2\text{CO}_3 + \text{Al}(\text{OH})_3$  at  $\text{pH}=9.5$

Calcination temperature ( $^\circ\text{C}$ )	Surface area ( $\text{m}^2/\text{g}$ )
650	163.89
800	57.78
950	125.36

Table 2 — Surface area measurement of commercial  $\text{LiAlO}_2$

Calcination temperature ( $^\circ\text{C}$ )	Surface area ( $\text{m}^2/\text{g}$ )
650	65.13
750	54.89
950	59.99

crystal structure and extrication of water and  $\text{CO}_2$  after the transformation of  $\text{CO}_3^{2-}$  and  $\text{Al}(\text{OH})_3$  that could probably have remained in crystal lattices. Another approach is the enhancement of the pores during the moving away of  $\text{CO}_2$  and water that could be remained in the structure at little amounts.

As a result of the surface area measurements, it was determined that the surface areas at all  $\text{pH}$ s at  $650^\circ\text{C}$  were high. If kept in mind that  $\text{LiAlO}_2$  phase was in alpha structure in XRD studies at this temperature and  $650^\circ\text{C}$  was an optimum operation temperature in MCFC and the surface area of  $\text{LiAlO}_2$  being high was an important parameter, it is thought that alpha  $\text{LiAlO}_2$  synthesized from  $\text{Li}_2\text{CO}_3 + 2\text{Al}(\text{OH})_3$  was successfully synthesized as an electrolyte support material used in molten carbonate fuel cell. When the results obtained were compared with the literature, it was seen that the values were higher<sup>5</sup>.

In the synthesis, it was tried to make  $\text{LiAlO}_2$  synthesis using four different equations. However, since the required objective was reached with the  $\text{LiAlO}_2$  synthesized from  $\text{Li}_2\text{CO}_3 + 2\text{Al}(\text{OH})_3$ , only

the results of LiAlO<sub>2</sub> synthesized from these compounds were included in this study.

### Conclusion

Aluminum has been examined as an economical and viable reinforcement for MCFC electrolyte matrices. The main mechanism of Al-reinforcement is found to be melting and phase transformation of the Al phase. The synthesis of LiAlO<sub>2</sub> was realized using four different equations. However, since the required objective was achieved with the LiAlO<sub>2</sub> synthesized from Li<sub>2</sub>CO<sub>3</sub> + 2Al(OH)<sub>3</sub>, only the results of LiAlO<sub>2</sub> (The largest surface area 163.89m<sup>2</sup>/g and calcinated at 650°C) synthesized from these compounds were included in this study.

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