

Influence of aluminum salt addition on in situ sintering of electrolyte matrices for molten carbonate fuel cells

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Abstract

Three aluminum salts are investigated as a sintering aid for the in situ sintering of electrolyte matrices for molten carbonate fuel cells (MCFCs). Only aluminum acetylacetonate shows a potential. At or above 420°C, aluminum acetylacetonate changes to Al₂O₃ and reacts with Li₂CO₃ in the electrolyte to produce γ -LiAlO₂. This reaction product forms necks between matrix particles. Necks grow with increasing sintering time and correspondingly, the mechanical strength of the electrolyte matrix shows an abrupt increase, starting at a sintering time of about 100 h until it levels off at about 250 h. The porosity of the matrices fabricated with aluminum acetylacetonate is in the range acceptable for use in MCFCs. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Fuel cells may be shut down occasionally, in the midst of their operation and this thermal cycling causes a special problem in a molten carbonate fuel cell (MCFC). The carbonate electrolyte, having existed in the molten state during operation, starts solidifying when the cell is switched off and cooled down to the liquidus temperature of the electrolyte. Due to the large volume increase on solidification, stresses build up in the matrix and may cause formation and propagation of cracks, which lead to significant gas cross-over between the two electrodes and, eventually, to decay in cell performance [1].

It is the common practice for the green sheet of matrix, usually fabricated by tape casting, to be assembled next to that of electrolyte in a stack of cells for impregnation, and sintered in situ during operation. The matrix is made mainly of fine γ -LiAlO₂ powder. Alumina fibres and/or coarse γ -LiAlO₂ particles are used as reinforcing additives. It has been reported [2–4] that the coarse particles limit crack propagation and that the fibres strengthen the matrix to prevent cracking [2–4]. These additives are supposed to become effective only if sintering is proceeded to a certain

extent and bonding between constituent particles is established. This cannot be accomplished quickly in the case of in situ sintering performed at relatively low temperatures and, therefore, there is a need for some sort of sintering aids.

In this study, three aluminum salts are examined as a sintering aid, but discussion is focused only on the results for the one judged to be the best. A composite electrolyte/matrix sheet is prepared for sintering experiments instead of two separate sheets. This product is intended to simplify the fabrication process, but sintering of the matrix may be influenced by the size of the electrolyte particles. Therefore, the electrolyte powder is ball-milled for size control before being mixed with the matrix powder and the effect of this pre-milling process is examined.

2. Experimental

It is expected that aluminum salts react with Li₂CO₃ in the electrolyte to produce a second phase, hopefully γ -LiAlO₂, and that this product interconnects matrix particles of the same phase which, thereby, improves the sinterability of electrolyte matrices.

Three aluminum salts from Aldrich (Table 1) were tried as sintering aids. Cold isostatic pressing (CIP), instead of tape casting, was used to fabricate green sheets of electrolyte matrices which were strong enough for mechanical strength

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Table 1
Physical characteristics of chosen aluminum salts

Al salts	Average particle size (μm)	Manufacturer
Aluminum isopropoxide $((\text{CH}_3)_2\text{CHO})_3\text{Al}$	4	Aldrich
Aluminum acetate $(\text{CH}_3\text{CO}_2)_2\text{AlOH}$	1	Aldrich
Aluminum acetylacetonate $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Al}$	0.1	Aldrich

tests to be conducted in their sintered state. The fabrication procedure is shown in Fig. 1. The aluminum salt was dissolved in toluene/ethanol solvent up to its solubility limit. This solution was placed in a nylon jar together with dispersant (corn oil) and powders of electrolyte and matrix, and then ball-milled for mixing.

The target composition of the electrolyte was 62 mol% Li_2CO_3 -38 mol% K_2CO_3 . Li_2CO_3 was added in excess, however, to compensate for that consumed by reaction with the aluminum salt. The average size of lithium carbonate particles was found to be $\sim 3 \mu\text{m}$. Potassium carbonate particles were too large for size analysis and presumed to be larger than $100 \mu\text{m}$. Therefore, the electrolyte powder was pre-milled for size reduction. Otherwise, there would be, during fuel cell start-up operation, viscous flow of the liquefied electrolyte for redistribution in the electrolyte matrix and this flow would retard the sintering process. Pre-milling was performed under the conditions that were concluded to be optimal in a previous study [5].

For microscopic observation or X-ray diffraction (XRD) analysis, coarse $\gamma\text{-LiAlO}_2$ powder (LSA-50) was used as the matrix material. Large particles of a single phase were thought to be assist the observation of necks, if any, formed between them during sintering or to recognize the second phase. For other purposes, a mixture of fine $\gamma\text{-LiAlO}_2$ powder (HSA-10) and reinforcing additives (LSA-50 and

alumina fibre, which had been commonly employed as the matrix material in our laboratory, was used.

The green sheet of electrolyte matrix was sintered in situ at 650°C for various times between 50 and 400 h. A three-point bend test was performed on the sintered sheet using UTM (Shimatsu, AGS-1000D) to measure its mechanical strength. The carbonate electrolyte was then removed from the sintered sheet, by application of a mixture of acetic acid and acetic anhydride (1:1 by volume), for porosity measurement and microscopic observation. The porosity was measured using Archimedes principle and microscopic observation was made by means of a scanning electron microscope (JEOL, JSM-5200). XRD experiments were performed twice, i.e. before and after removal of the electrolyte, using a Rigaku diffractometer (Geigerflex D/MAX-II A).

3. Results and discussion

Among the three salts, aluminum acetate and aluminum isopropoxide did not dissolved sufficiently in the toluene/ethanol solvent to produce, by the reaction with Li_2CO_3 , a sufficient amount of the second phase for necking. A scanning electron micrograph of a matrix fabricated with aluminum acetate and sintered for 100 h is given in Fig. 2. No trace of neck formation between matrix particles can be seen. As expected from this, the use of aluminum acetate did not give any extra mechanical strength to the sintered electrolyte matrix. This was also the case for aluminum isopropoxide.

Aluminum acetylacetonate, on the other hand, was dissolved plentifully in the solvent and showed promise as a sintering aid. Scanning electron micrographs for the matrices fabricated with aluminum acetylacetonate and sintered for 50, 100, or 200 h are presented in Fig. 3. At

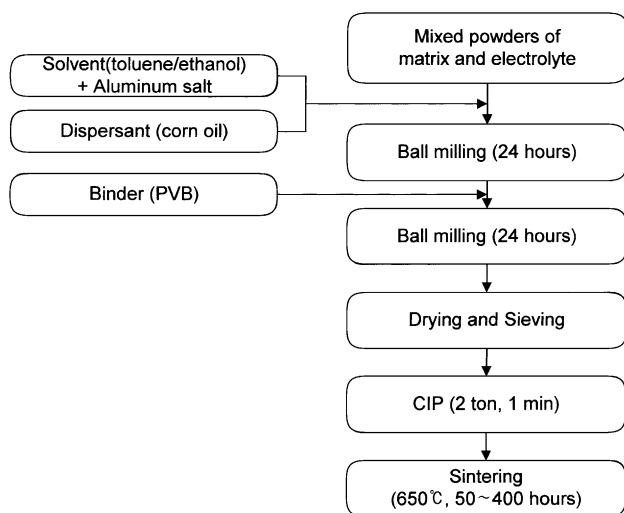


Fig. 1. Flowchart of fabrication process of electrolyte matrices by CIP, using aluminum salt as a sintering aid.

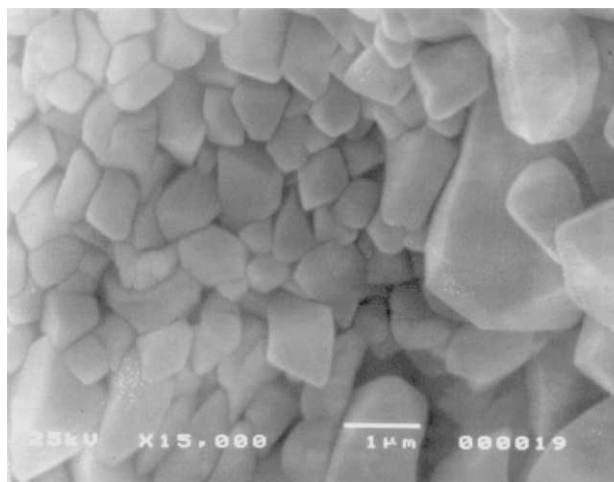


Fig. 2. Scanning electron micrograph of a matrix produced using aluminum acetate as a sintering aid.

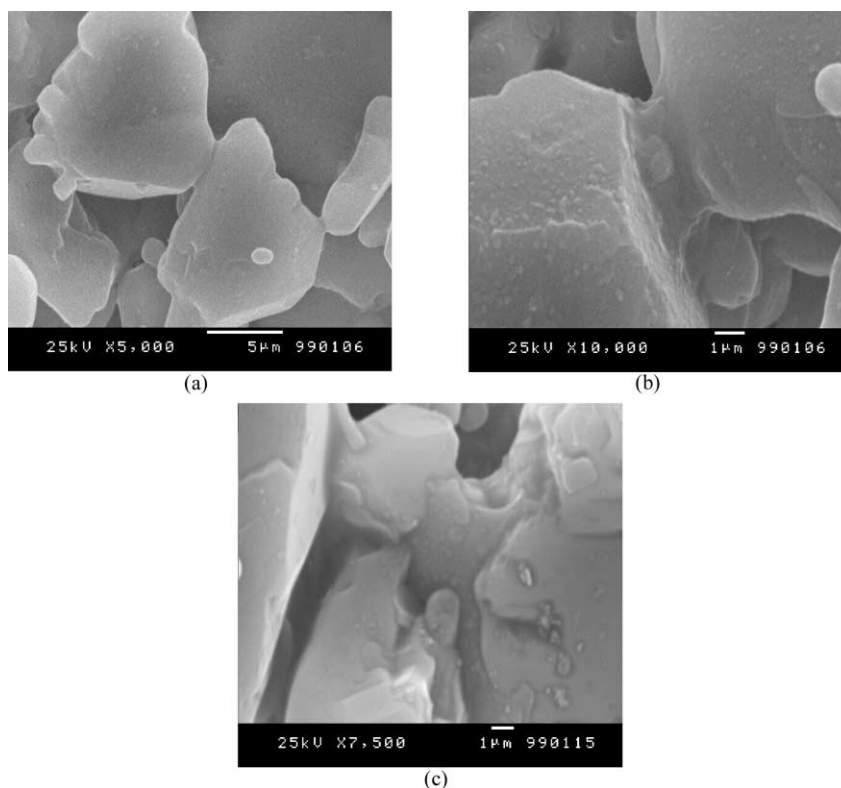


Fig. 3. Scanning electron micrographs of matrices prepared with aluminum acetylacetonate and sintered for (a) 50, (b) 100, (c) 200 h.

50 h, neck formation appears to have already started. The necks grow with increase in sintering time and at 200 h some of the matrix particles appear to be united together into a large mass. This phenomenon suggests that some reaction must have occurred during sintering and have produced a second phase which is responsible for neck formation.

Further discussion will be made later on the details of the reaction.

To identify the second phase, XRD analysis was performed on the electrolyte matrix sintered for 100 h, see Fig. 4(a). Peaks for lithium carbonate, potassium carbonate and γ -LiAlO₂ are detected. A careful search was made

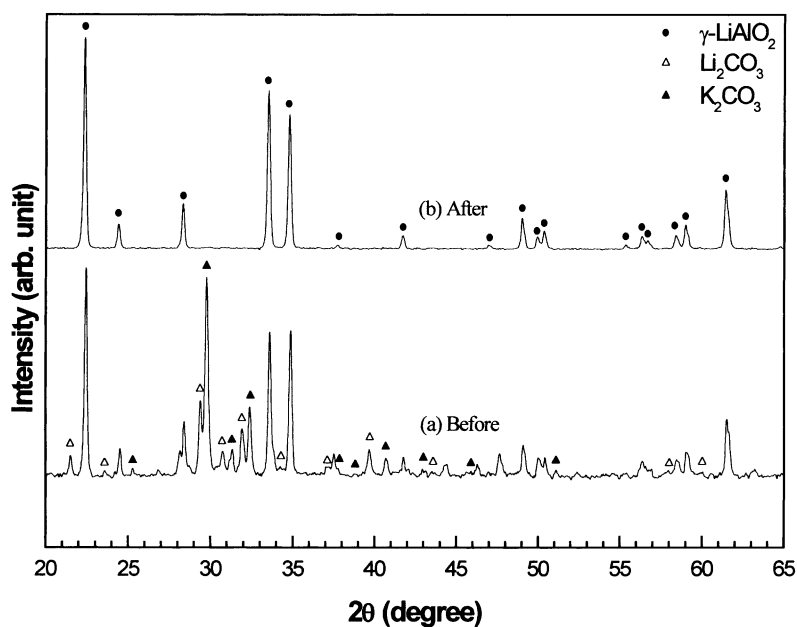


Fig. 4. XRD patterns for an electrolyte matrix (a) before and (b) after removal of electrolyte.

throughout the pattern for other phases which might possibly form during sintering. The pattern, however, is very much crowded with peaks and also shows a large variation in intensity, probably due to the carbonate electrolyte. Therefore, an XRD pattern was obtained once again for the same electrolyte matrix, but this time after removal of the electrolyte. A single phase of γ -LiAlO₂ was recognized from the pattern, as shown in Fig. 4(b). So, the only possibility is that the reaction product is γ -LiAlO₂, the same phase as the matrix, as we expected earlier.

3.1. Pre-milling of electrolyte powders

As already mentioned, the electrolyte powder was ball-milled before being used for fabrication of the electrolyte matrix. A previous study has shown [5] that pre-milling of the electrolyte powder will reduce its particle size. It was thought that the reduction of particle size would, in turn, prevent unnecessary flow of the liquified electrolyte and help matrix particles in the powder compact to remain and thus facilitate sintering or neck formation. This conjective had to be verified experimentally and, accordingly, electrolyte matrices were prepared once again using as-received electrolyte powder without pre-milling. Scanning electron micrographs of the matrices are presented in Fig. 5. For a sintering time of 100 h, neck is barely formed between two large matrix particles. This is in contrast to the distinct neck formation shown in the corresponding micrograph of Fig. 3. Even after 200 h, the particles are still poorly interconnected over a very small portion of their surfaces.

3.2. Mechanical strength

The in situ sintering of electrolyte matrices should give sufficient strength in a short period of time for their thermal cyclability. The mechanical strength plotted against sintering time for three different electrolyte matrices is shown in Fig. 6. Two of these matrices were made of LSA-50, one with aluminum acetylacetonate and the other without, and the third was made of a mixture of HSA-10, LSA-50, and alumina fibres also using aluminum acetylacetonate as a sintering aid. When two LSA-50 matrices are compared, the role of the aluminum salt in the process of sintering of electrolyte matrices can be clearly realized. The mechanical strength shows an abrupt increase starting at a sintering time of about 100 h until it levels off at about 250 h for the one with aluminum salt, while there is almost no variation of mechanical strength with sintering time for the other. The composite matrix, when fabricated with aluminum salt, shows a similar trend as the corresponding LSA-50 matrix, but has higher strength at all sintering times.

3.3. Reaction mechanism

The necks observed between matrix particles in Fig. 3 indicates that some reaction has indeed occurred during

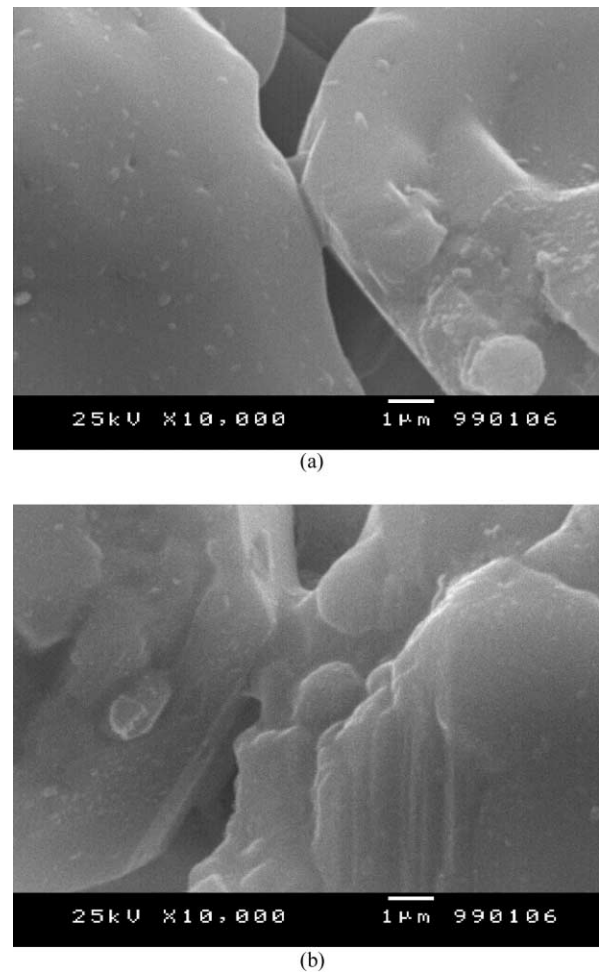


Fig. 5. Scanning electron micrographs of matrices prepared with as-received electrolyte powder without pre-milling and sintered for (a) 100 and (b) 200 h.

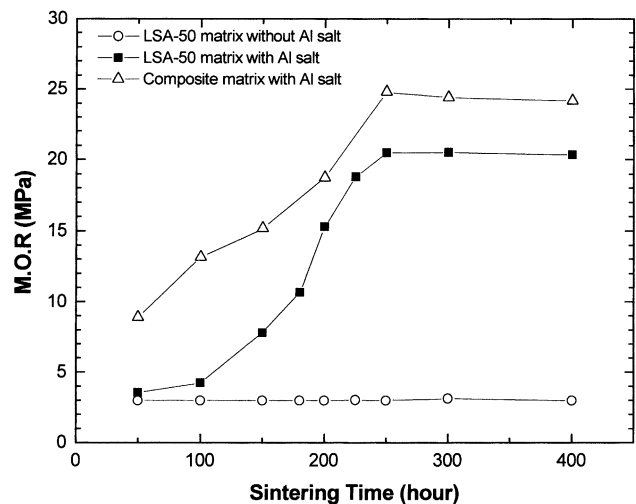


Fig. 6. Variation of modulus of rupture (MOR) with sintering time for three different matrices. $MOR = 3PL/2WH^2$, where P = load (kgf); L = length of specimen; W = width of specimen; H = height of specimen.

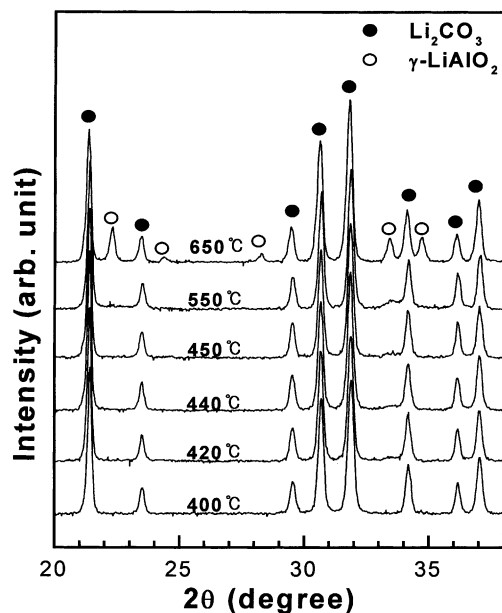


Fig. 7. XRD patterns of Li_2CO_3 /aluminum acetylacetonate mixture heated at various temperatures for 5 h.

sintering. Furthermore, according to the data in Fig. 4, the only possibility for the reaction product is $\gamma\text{-LiAlO}_2$. The reaction mechanism is, however, not yet known. Two extra experiments were performed in order to elucidate the reaction mechanism. In the first experiment, aluminum acetylacetonate and Li_2CO_3 , which are presumed to be two reactants, were mixed together and held at various temperatures in the range of 400–650 °C for 5 h to react sufficiently with each other. The reaction products were identified from the XRD patterns shown in Fig. 7. At 650 °C, several peaks for the $\gamma\text{-LiAlO}_2$ phase can be easily recognized, together with those for Li_2CO_3 . At temperatures below 650 °C, however, these peaks are not in detectable sizes except for the one at $2\theta \approx 33.5^\circ$ which grows with increase in temperature starting at 420 °C. Thus, this seems to be the temperature at which $\gamma\text{-LiAlO}_2$ starts to be produced by the reaction of aluminum acetylacetonate with Li_2CO_3 . The question then arises: ‘do aluminum acetylacetonate or Li_2CO_3 remain or change into other phases when they react with each other?’ The answer to this question was obtained by the second experiment in which aluminum acetylacetonate (or Li_2CO_3) was heated at 420 °C for 5 h and the bonding state of aluminum (or lithium) was analyzed using the Al-2p (or Li-1s) photoelectron peak. The photoelectron spectra were measured in an XPS spectrometer (VSW-ARIESARSC 10MCD 150) using a monochromated Mg $K\alpha$ X-ray source. The Al-2p and Li-1s peaks are shown in Fig. 8 and their binding energies were found to be, after calibration with respect to C-1s, 74.4 and 55.2 eV, respectively. The position of the Al-2p peak is indicative of the formation of Al_2O_3 , but that of Li-1s represents the bonding state of lithium in Li_2CO_3 . This shows that aluminum acetylacetonate has changed into Al_2O_3 whereas lithium

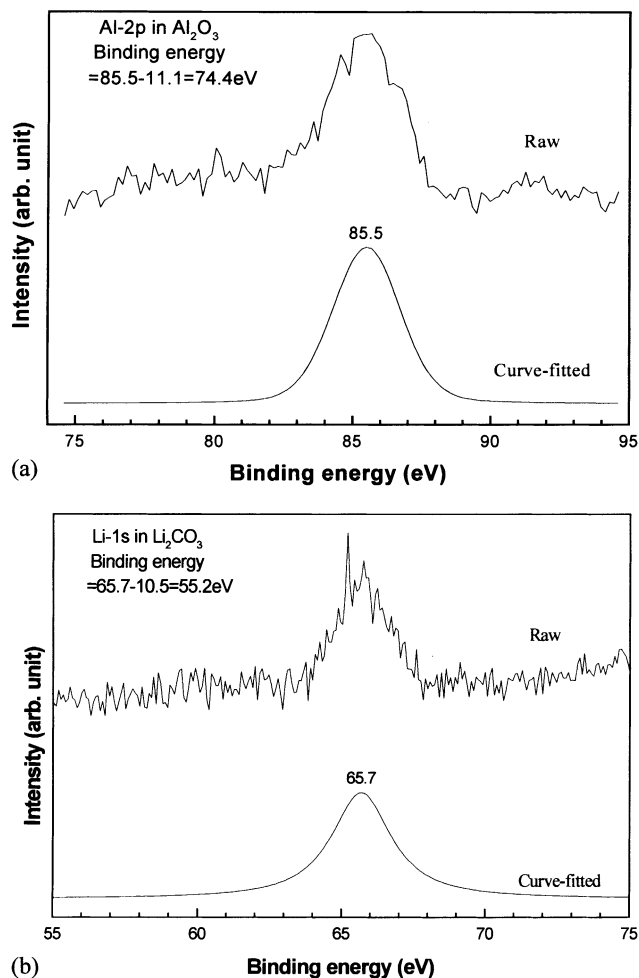
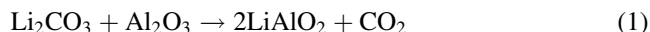


Fig. 8. XPS spectra of (a) aluminum acetylacetonate and (b) Li_2CO_3 heated at 420 °C for 5 h.

carbonate remains unchanged at 420 °C. The reaction mechanism can therefore be summarized as follows. At or above 420 °C, aluminum acetylacetonate converts to Al_2O_3 which reacts with Li_2CO_3 to produce LiAlO_2 , i.e.



3.4. Porosity

Sintering of a powder compact is accompanied by pore shrinkage as well as pore shape change and grain growth. Thus, the sinterability of a porous structure is generally improved at the expense of reduction of pore space. To be used in a MCFC, however, the matrix must have a porosity in the range 50 to 70% for electrolyte retention. The electrolyte matrices fabricated with aluminum acetylacetonate had to be checked if they had porosities in the acceptable range. Porosity versus sintering time curves for the composite and LSA-50 matrices are given in Fig. 9. The porosity decreases with increasing sintering time for both matrices until it stabilizes at a constant value. The values of porosity

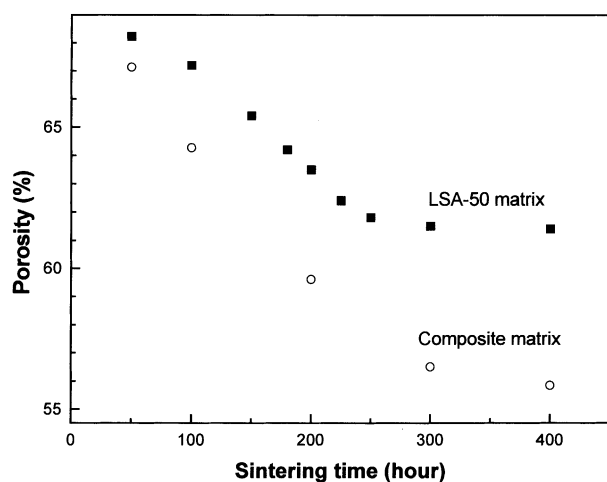


Fig. 9. Variation of porosity with sintering time for composite and LSA-50 matrices.

after stabilization are 56 and 61.5%, respectively, for the composite and LSA-50 matrices.

4. Conclusions

Aluminum acetylacetonate, aluminum acetate and aluminum isopropoxide have been examined as a sintering aid for MCFC electrolyte matrices and the following observations have been made.

1. Aluminum acetylacetonate shows promise as the sintering aid, whereas aluminum acetate and aluminum isopropoxide does not.

2. At or above 420°C, aluminum acetylacetonate changes into Al_2O_3 and reacts with Li_2CO_3 to produce LiAlO_2 . This reaction product forms necks between the matrix particles.
3. Necks grow with increase in sintering time and, correspondingly, the mechanical strength of the electrolyte matrix displays an abrupt increase starting at about 100 h and levels off at about 250 h.
4. Pre-milling of electrolyte powders facilitates the in situ sintering of electrolyte matrices.
5. The porosity of matrices fabricated with aluminum acetylacetonate is in a range which is acceptable for use in a MCFC.

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