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Reinforcement of the MCFC matrix by Al-based additives: effect of lithiation

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Abstract

The matrix material in a Molten Carbonate Fuel Cell, usually LiAlO_2 , has an important role in the ionic conduction, gas sealing and electrolyte retention. To avoid cracking, this material has been reinforced with various additives, mostly Al-based, which are subject to *in situ* lithiation. In this work, matrices were systematically synthesized through a fast and more environmentally friendly route and characterized, with two types of reinforcing agent, either Al powder or Al_2O_3 fibers, both with and without carbonates. Then, a comparative analysis was done, in terms of mechanical strength and porosity, on the effect of adding Al powder and Al_2O_3 fibers and their subsequent lithiation. This reaction was found to be quantitative after 50 h at 650 °C, and matrices with reinforcing agent and carbonates featured increased mechanical strength by a factor up to 2 compared to matrices with only reinforcing agent, reaching 0.61 kgf.mm⁻². Al powder was also found to be better suited than Al_2O_3 fibers for addition in a matrix, also contributing to enhance the porosity, particularly after lithiation.

Keywords: MCFC, matrix, aluminum, alumina, reinforcement, lithiation.

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I- Introduction

The molten carbonate fuel cell (MCFC) is an electrochemical energy conversion device that features interesting advantages compared to other types of fuel cell, namely high efficiency, fuel flexibility and enhanced kinetics due to the working temperature of 650 °C, fuel flexibility. It is now a mature technology with a 60 MW power plant installed in South Korea [1]. This device, due to the specific properties of molten carbonates, can also be considered for CO₂ capture and valorization (CCV) processes [2-6].

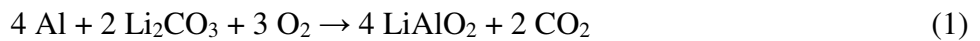
Among the components of MCFCs, the matrix plays a key role. It has to retain the electrolyte, based on lithium carbonate eutectics, while ensuring electronic insulation and keeping a high ionic conduction between the electrodes. Gas sealing is also a major property that the matrix has to address. Furthermore, this material has to possess good porosity, usually between 50 and 70 %, with good mechanical strength [7].

The matrix is usually made of LiAlO₂. However, there are some well-known issues in the MCFC, such as cracking during either heat-up of the cell or operation, leading to performance losses, gas crossover and long-term instability.

At the beginning of the research on MCFC matrix, the most used material was γ -LiAlO₂, due to it being the high-temperature stable phase and having good mechanical properties [8, 9]. However, an important research effort has been done in the literature on the stability of LiAlO₂ phases in the specific MCFC conditions, including phase transformations and possible particle growth. This is a difficult topic, as evidenced by the contrasting results obtained, depending on temperature and gas atmospheres, one single matrix being subject to both cathode and anode atmospheres inside the MCFC cell. Indeed, nowadays the α -LiAlO₂ phase is widely considered to be the more stable phase with less particle growth in molten carbonates at a temperature of 650 °C under CO₂-rich atmospheres [7, 10-12]. This is however not true under air, where γ -LiAlO₂ is more stable [12]. In addition, Heo *et al.* have recently shown that the gamma phase was stable in hydrogen-rich atmospheres and the alpha phase transformed to gamma in the same conditions [13, 14].

Some authors considered mixtures of both allotropic forms, and the stability then depends on the size of the particles of each of them. It has been stated that the smaller particle phase undergoes transformation through a dissolution/precipitation mechanism, similar to Ostwald ripening [10]. With the same particle size for both phases, results remain not fully conclusive.

In order to improve the mechanical properties of the MCFC matrix, most of the approaches have been through the use of reinforcing agents to prevent cracking. Usually, the reinforcing agents are Al-based, such as LiAlO₂, Al, Al₂O₃, and have various morphologies. Large particles have been used as a direct crack inhibitor. Two US patents have been developed on the synthesis of a matrix with large Al₂O₃ and LiAlO₂ particles that were more than 50 microns in size [15, 16]. Al particles have been used extensively, and the mechanical strength of Al-reinforced matrices dramatically increased, being multiplied by 3 compared to the bare LiAlO₂ matrix [9, 17]. It has also been found that the Al particles react during MCFC operation through reaction 1.



As the electrolyte loss is already an issue limiting the durability of the MCFC, the use of such particles as reinforcing agents requires additional Li₂CO₃ to compensate the lithiation reaction.

The LiAlO₂ and Al₂O₃ additives were also used in the form of fibers. Then, the reinforcing mechanism is a bit different than that with the addition of particles, the cracks are deflected by the fibers and propagate at parallel or at right angles to them, and the mechanical properties are also improved thanks to the fibers' resistance to pullout [18]. For both types of fibers, matrices with higher mechanical properties were obtained [18, 19]. However, in the case of Al₂O₃, a lithiation reaction similar to that of Al particles takes place during MCFC operation, as depicted by reaction 2.



Finally, the use of an Al foam has recently been reported as promising [20].

In the literature, the effect of such reactions has not been fully considered, either because carbonates were not systematically added, or because the amount of Li₂CO₃ added was insufficient to completely achieve the lithiation reactions [9, 17]. However, a study on possible additional lithium sources for the matrix material highlighted that for MCFC operation, the use of LiOH instead of Li₂CO₃ is preferable due to a lower melting point and because it will not alter the carbonate composition of the electrolyte and lessen the likelihood of void formation [21].

Our work directly analyzes and compares two Al-based additives, Al powder and alumina fibers, the lithiation reaction in both cases resulting in LiAlO_2 . Herein, the matrix material is studied by itself, and the Li source is Li_2CO_3 . The completion of the reaction was ensured through an adapted heat-treatment and voids were not observed. In addition, the effect of lithiation is thoroughly addressed as the carbonate amount was added stoichiometrically in order to obtain quantitative reactions with the additives (reactions 1 and 2). Adequate addition of carbonates is also key to avoid unnecessary electrolyte loss. Matrices were synthesized with various Al contents, from 5 % to 30 % of total powder, or 9.4 % Al_2O_3 fibers, with and without carbonates. The alumina percentage was calculated in order to have the same number of moles of LiAlO_2 formed after lithiation as the matrix with 5 % Al. In both cases, the synthesis protocol was the same. The matrices without carbonates could represent the initial state at the start-up of the MCFC cell, prior to reactions 1 and 2. Besides, carbonate amount was each time added stoichiometrically to ensure full lithiation of the additive considered, the completion of the reaction being confirmed by XRD.

II- Experimental

The matrices in this work were synthesized via tape-casting, inspired from the protocol of Kim *et al.* [17]. The device used was supplied by Fiaxell. A slurry was obtained by mixing the base $\gamma\text{-LiAlO}_2$ powder (Alfa Aesar), the additives: Al powder (Merck, > 90 %), or Al_2O_3 fibers (synthesis protocol given afterwards), a binder (Polyvinylbutyral or PVB, Butvar B-98, Merck), a plasticizer (Polyethylene glycol or PEG, Merck), a dispersant (Zetasperse, ININ) and a defoamer (Surfynol, ININ) with the solvent (butanol and isopropanol, 50 %/50 % weight, VWR Chemicals). When Li_2CO_3 (Merck, > 99 %) was used, the quantity was adjusted to fully consume the Al or Al_2O_3 . All used materials in the slurries are provided in table 1.

The mixing was done in a given order: indeed, the binder and plasticizer were added to the slurry only after 4 h of ball milling of all the other components, according to the method given in figure 1. Then, after another ball milling for 18 h, the slurry was tape-cast on a Mylar film substrate (Doctor Blade height 1 mm), dried and removed. This synthesis process is faster than most reported in previous studies [7, 9, 17]. Besides, it is more environment-friendly as it does not feature toluene as solvent.

Table 1- Materials used for tape-casting of the matrix

Function	Compound	Quantity (weight %)
Raw powders (with additives)	LiAlO ₂ , Al powder, Al ₂ O ₃ fiber, Li ₂ CO ₃	36.3
Dispersant	Zetasperse	1.1
Binder	PVB	9.1
Plasticizer	PEG	5.8
Defoamer	Surfynol	0.5
Solvent	Butanol	23.6
	Isopropanol	23.6

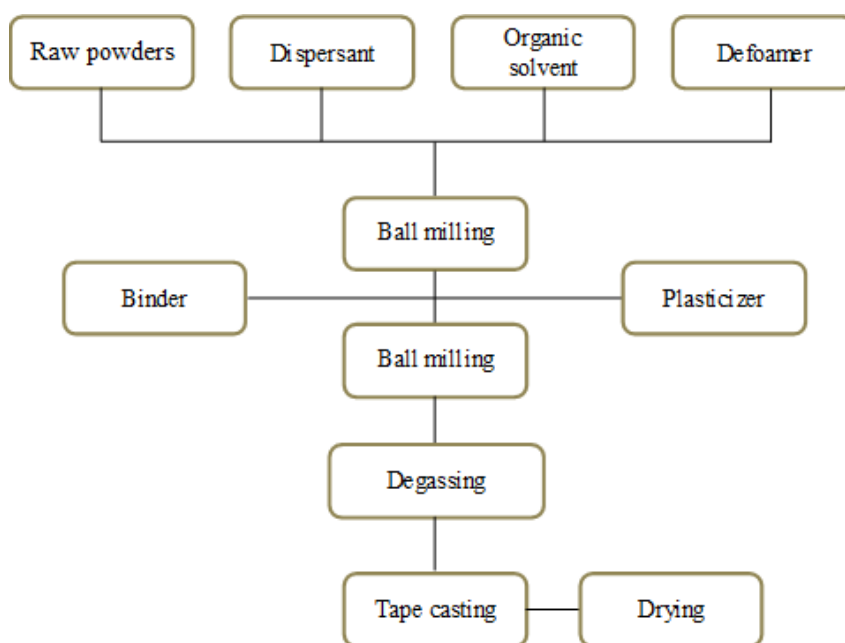


Fig. 1- Synthesis protocol for the matrix material.

After drying, the obtained matrices were burnt-out in air according to the heating program provided in table 2. This program was obtained from TGA/DSC data that is not provided here, which was obtained with a Setaram Setsys Evolution device between 40 °C and 800 °C. All temperatures were reached with a 3 °C min⁻¹ ramp.

Table 2- Heating program (in air) for the matrix

Temperature (°C)	Dwell time (h)
140	2
160	2
280	2
340	2
380	1
420	2
480	1
650	50

The Al₂O₃ fibers used in this study were synthesized from the protocol given by Yang *et al.* [22]. A mercury-based solution was obtained by dissolving 0.5 g of HgCl₂ (Merck, > 99 %) in 100 mL of Milli-Q water. A high purity Al plate was then immersed in this solution for 5 minutes and then taken out and left in air. After a while, the grown Al₂O₃ fibers were gathered and heat-treated at 1250 °C for 2 h to obtain α -Al₂O₃.

The characterizations were performed on burnt-out matrices unless stated otherwise.

Crystallographic analyses of the matrices were carried out by X-Ray Diffraction, using a PANalytical XPERT Pro diffractometer, according to the following parameters : Cu anticathode ($\lambda_{K\alpha, Cu} = 1.5406$ nm), I = 40 mA, V = 45 kV, from $2\theta = 10$ to 70° , using a 0.026° step (scan speed $0.05^\circ s^{-1}$).

Mechanical properties were investigated by 3-point bending tests, using a Universal testing machine, model 112 (GT-Test GmbH), with a span at 14 mm. The sample was deflected at the rate of 1 mm min^{-1} under the pressure from a stylus connected to a 20 N load cell.

SEM images were obtained using a Zeiss Leo1530 microscope working at 2.5 kV.

III- Results and discussion

XRD analysis

The synthesized matrices, with and without carbonates, were analyzed by XRD in order to determine the crystallographic phases and follow the lithiation process. In the following results, the base LiAlO_2 matrix is referred to as the bare matrix, and the reinforced matrices are named after the nature and amount of reinforcing agent they possess, *e.g.* the LiAlO_2 matrix reinforced with 30 % Al is called 30 % Al.

Figure 2 presents X-ray diffractograms of a matrix with the highest amount of reinforcing agent and carbonates (30 % Al + Li_2CO_3) with various dwell times at 650 °C in air.

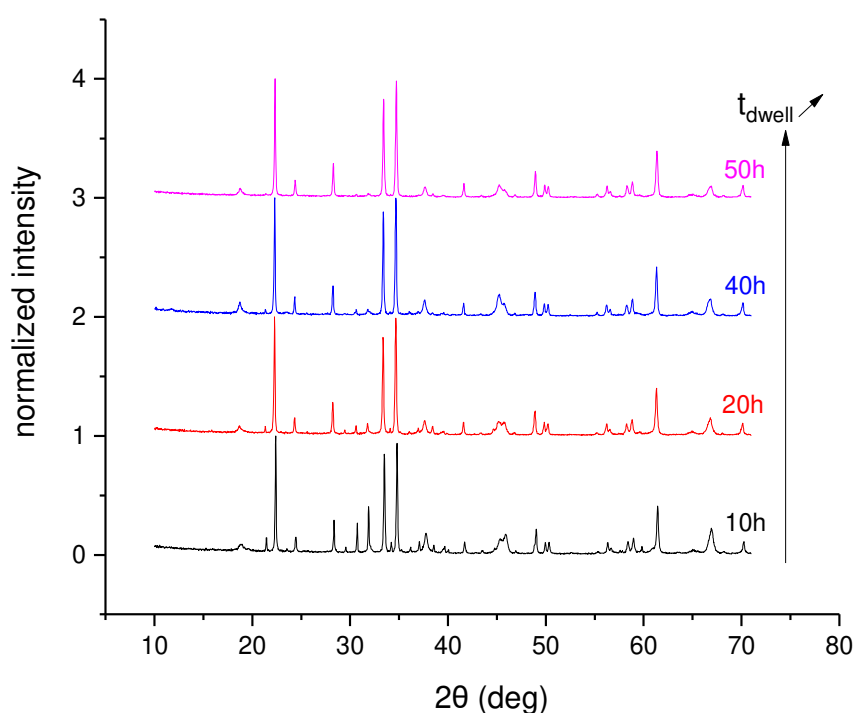


Fig. 2- Diffractograms of 30 % Al + Li_2CO_3 samples for various dwell times at 650 °C in air.

As can be seen from the triplet at 29.6 °, 30.7 ° and 31.9 ° corresponding to planes (111), (-202) and (002) of lithium carbonate and the peaks at 38.4 °, 44.7 ° and 65.0 ° corresponding to planes (111), (200) and (220) of Al, the lithiation reaction is not quantitative for 10 h at 650 °C, contrarily to what is reported in the literature [9]. With respect to the mentioned study, we used a higher amount of lithium carbonate for reaction 1 to be quantitative. The higher melting point of Li_2CO_3 , used here, compared to LiOH , used as lithium source in another study [21], might explain the longer reaction time that we obtained. This was achieved in 50 h at 650 °C, which is the previously given dwell time, that was considered for this work.

Diffraction patterns for the Al base powder, and Al-reinforced matrices, with and without Li_2CO_3 , are given in figure 3.

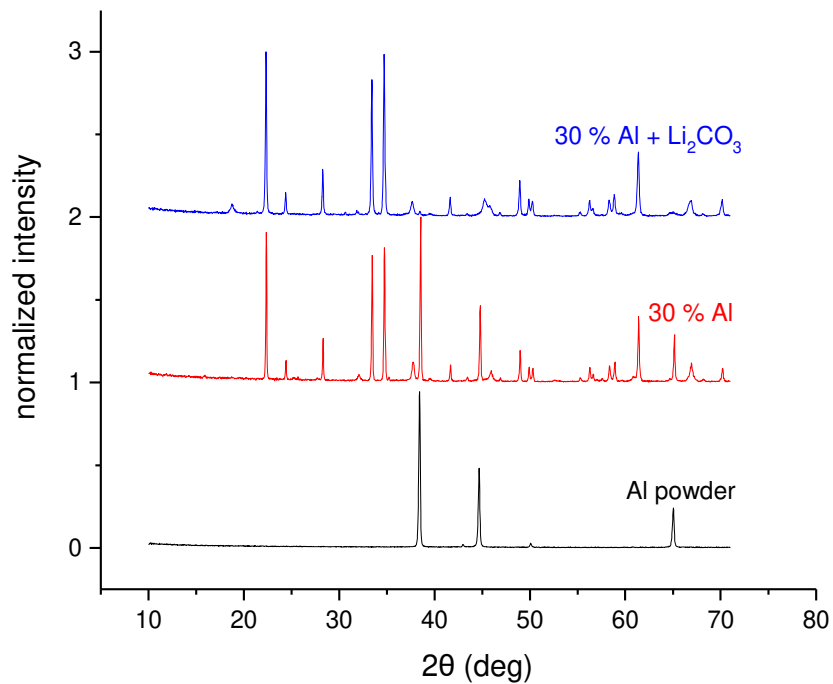


Fig. 3- Diffraction patterns for base Al powder and Al-reinforced samples with and without Li_2CO_3 .

After heat treatment in air, an aluminum phase in the matrix without carbonates remained, which is evidenced by the intense peak of metallic Al at 38.4 °, but also peaks at 44.7 °, and

65.0 °, corresponding to planes (111), (200) and (220). These peaks disappear when carbonates are present, indicating reaction 1 (formation of LiAlO_2) has occurred.

As for Al_2O_3 fibers used as additives, the diffractograms for the corresponding matrices are given in figure 4.

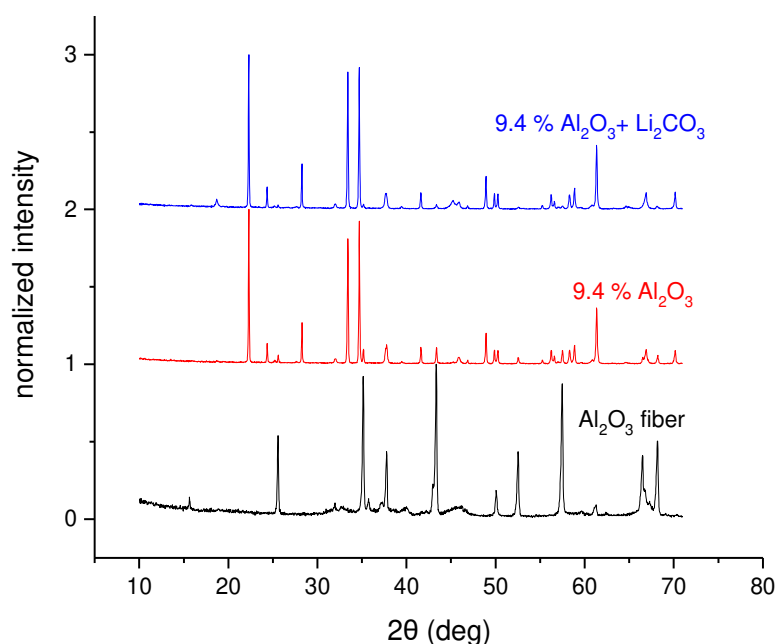


Fig. 4- Diffractograms for Al_2O_3 fibers and Al_2O_3 -reinforced samples with and without Li_2CO_3 .

For the matrices containing fibers and no carbonates, after burn-out, the alumina phase is unchanged, as evidenced by the common peaks due to Al_2O_3 between the fibers and the matrix containing fibers, at 25.5 °, 35.7 °, 43.4 °, 57.5 °, 66.4 ° and 68.2 ° corresponding to planes (012), (104), (113), (116), (024) and (030) of $\alpha\text{-Al}_2\text{O}_3$. This is more expected as alumina should be stable at this temperature under air. When lithium carbonate is also present, the lithiation reaction appears fully quantitative during burn-out, as these peaks have once more disappeared from the diffractogram of the 9.4 % $\text{Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3$ matrix.

Mechanical properties

The matrices were also tested for their mechanical properties thanks to 3-point bending test. The results are given in kgf.mm^{-2} , with $1 \text{ kgf.mm}^{-2} \approx 9.8 \text{ MPa}$.

Table 3- Bending strength of the matrix materials

Sample	Flexural strength (kgf.mm^{-2})
Bare matrix	0.07
5 % Al	0.32
10 % Al	0.13
20 % Al	0.22
30 % Al	0.38
9.4 % Al_2O_3 fibers	0.20
5 % Al + Li_2CO_3	0.61
10 % Al + Li_2CO_3	0.16
20 % Al + Li_2CO_3	0.45
30 % Al + Li_2CO_3	0.61
9.4 % Al_2O_3 fibers + Li_2CO_3	0.60

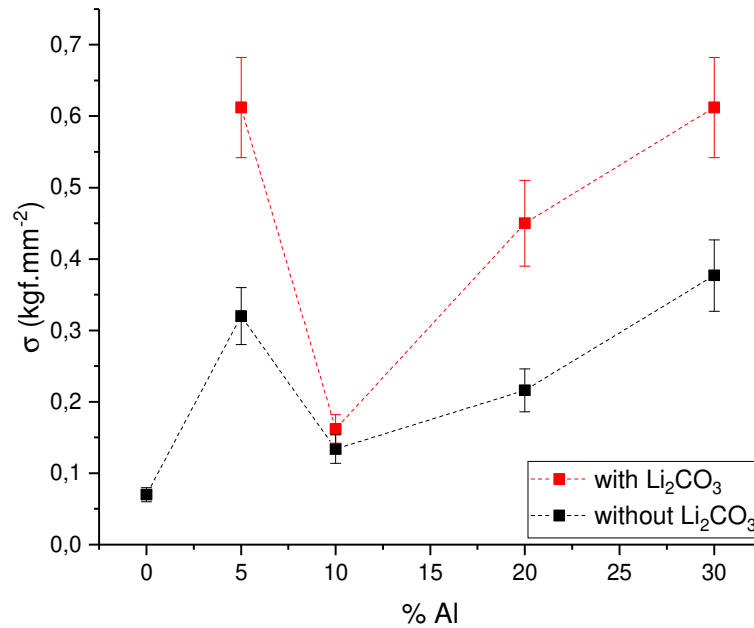


Fig. 5- Bending strength of Al-reinforced samples, with and without carbonates. The points are connected for better readability.

Without additives, the bending strength of the bare matrix was found to be 0.07 kgf.mm⁻². The addition of aluminum clearly improves mechanical strength of the samples. Indeed, all the samples with aluminum have a greater bending strength than that of the bare matrix. For 30 % Al, it is multiplied by 5. It is possible to notice that for 5 % Al, the bending strength is very high at 0.32 kgf.mm⁻², higher than for 10 % and 20 % Al, and close to the maximum value of 0.38 kgf.mm⁻² for 30 % Al. There seems to be a local maximum at 5 % Al, then the bending strength drops and gradually improves back from 10 % to 30 % Al. This interesting trend was also observed in the literature: a global maximum was found at 4 vol% Al added, then the bending strength decreased [9]. For higher percentages of additive, the base microstructure might be too altered by the Al phase, lowering the mechanical resistance of the material. In our case, only at 30 % Al is the same resistance reobtained.

The lithiation reaction, and resulting LiAlO₂, has a beneficial effect, as nearly all matrices with additive + carbonate are much more resistant than the ones only featuring the additive. The same trend as the case with only Al added can be observed, with a local maximum for 5 % Al + Li₂CO₃, then a drop at 10 % Al + Li₂CO₃ and gradual increase. The highest bending

strength values obtained were for the 5 % Al + Li₂CO₃ and 30 % Al + Li₂CO₃, around 0.6 kgf.mm⁻², which is 9 times higher than for the bare matrix.

In the literature, the use of Al without carbonates yielded at best bending strengths around 0.2 or 0.3 kgf.mm⁻² [9, 17], and 0.7 kgf.mm⁻² with carbonate [9], which is similar to what is obtained in our study (0.38 kgf.mm⁻² for 30 % Al and 0.61 kgf.mm⁻² for 30% Al + Li₂CO₃). However, the difference in the heat-treatment process has to be taken into account as it can change mechanical strength: it has indeed been shown that for heat treatment times longer than 50 h, the flexural strength of matrices usually decreases [9].

The influence of the other additive considered, alumina fibers, is presented in figure 6.

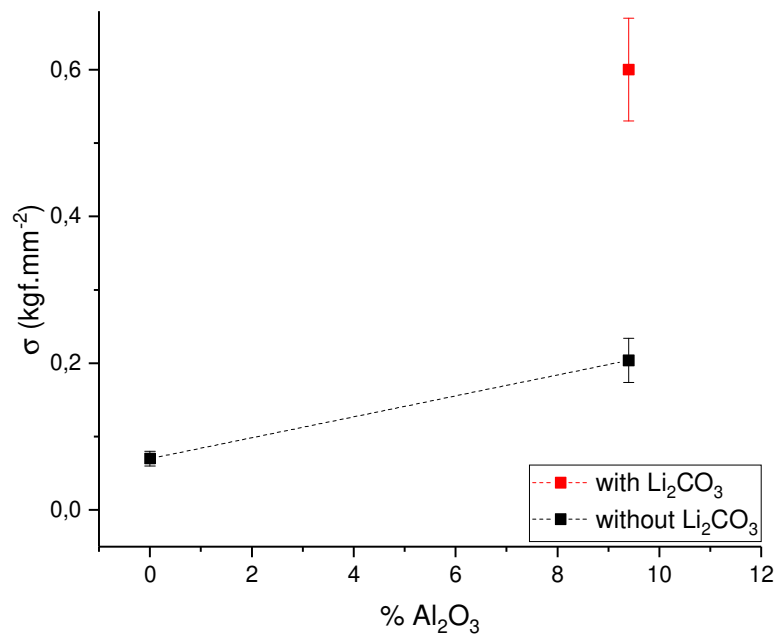


Fig. 6- Bending strength of Al₂O₃-reinforced samples, with and without carbonates.

The fibers also improve the flexural strength of the matrix, and lithiation is once more greatly beneficial. Results from the literature with fibers vary: values of 0.15 kgf.mm⁻² to 0.2 kgf.mm⁻² were obtained by a research group [18, 23], and above 2 kgf.mm⁻² by another, though in this case, the bare matrix already appeared extremely resistant [19].

As the 9.4 % Al₂O₃ + Li₂CO₃ matrix has the same amount of LiAlO₂ stemming from lithiation than the 5 % Al + Li₂CO₃, it is coherent to directly compare the values of bending strength obtained: with carbonates they are the same, but without, the Al-reinforced matrix is

better (0.32 kgf.mm^{-2} vs 0.20 kgf.mm^{-2}). This is all the more important as the samples with additives and no carbonates mimic the structure of the matrix at the start-up of the MCFC cell, which is a step in the MCFC lifetime that is known to induce cracking [7, 9, 24].

Thus, both Al particle and Al_2O_3 fiber addition enhance mechanical strength of the matrix. However, in terms of strength gained *versus* number of moles added, Al particles are more advantageous than Al_2O_3 fibers, on top of being easier to obtain.

Microstructure

For its specific role in the MCFC, the matrix microstructure is important. Indeed, to house and retain the electrolyte without loss, it has to feature a certain porosity and pore structure. Conventionally, the matrix has to feature porosity around 50% to 70% and a pore size below $1 \mu\text{m}$ for good electrolyte retention [7, 24].

SEM images of some samples are provided in figure 7.

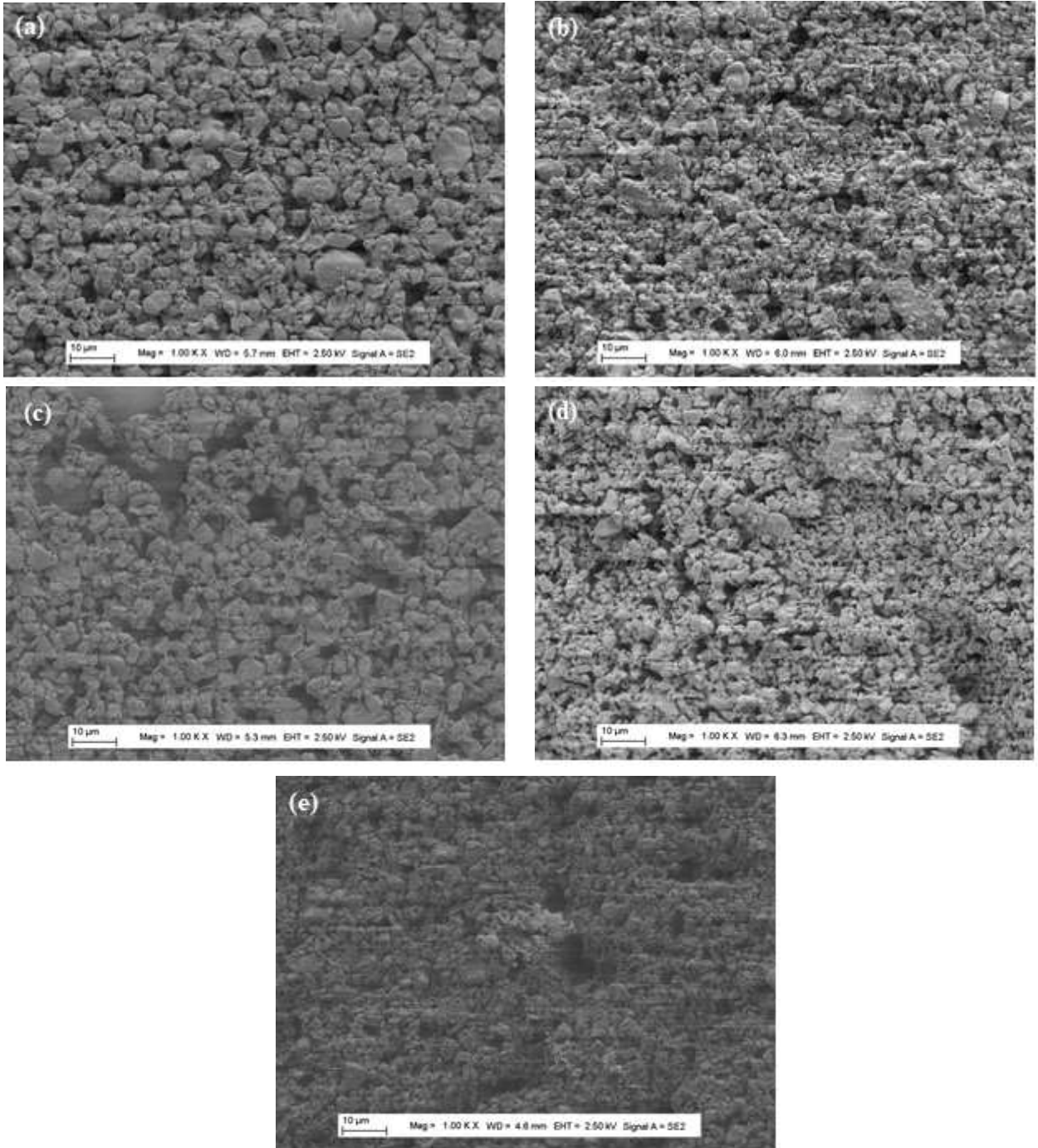


Fig. 7- SEM images of bare matrix (a), 5 % Al + Li_2CO_3 (b), 10 % Al (c), 10 % Al + Li_2CO_3 (d) and 9.4 % Al_2O_3 + Li_2CO_3 (e).

When additives are used, particularly after lithiation, the overall granulometry is finer, which can particularly be noticed by comparing 10 % Al and 10 % Al + Li_2CO_3 (figure 7c and 7d). Coarser particles can indeed be seen on the bare matrix surface and on the 10 % Al sample,

but not on the others. Though bigger pores are still visible, the overall pore size also shrinks and is below 1 μm for reinforced matrix materials.

As for the porosity in itself of the synthesized matrices, it was obtained through weighing, and comparison of density. The values are provided in table 4.

Table 4- Porosity values of the samples

Sample	Porosity (%) ± 3
Bare matrix	47
5% Al	51
10% Al	58
20% Al	62
30% Al	62
9.4% Al_2O_3 fibers	56
5% Al + Li_2CO_3	58
10% Al + Li_2CO_3	65
20% Al + Li_2CO_3	68
30% Al + Li_2CO_3	66
9.4% Al_2O_3 fibers + Li_2CO_3	51

All the matrix materials considered in the study have a porosity corresponding to the requirements for use in the MCFC. In general, the porosity increases with additive amount. In the case of Al, a previously reported trend is that its addition increases porosity while decreasing pore size, which is consistent with this work [9]. Indeed, the low melting point of Al and its ability to sinter tends to shrink pores. Naturally, these parameters also depend on heat-treatment process and particle size of the additive. In the case of fibers, a decrease in porosity has been previously observed but with a higher fiber amount [23]. However, the lithiation effect on both Al and Al_2O_3 is different. For Al, lithiation increases the porosity,

but for Al_2O_3 the porosity seems to decrease while remaining comparable. Overall, it can be stated that lithiation tends to improve the porosity, while decreasing pore size due to freeing of pores and smaller particles resulting from this reaction.

IV- Conclusion

Matrix materials were synthesized with a short, and more environmentally-friendly procedure with two different Al-based additives: Al powder and Al_2O_3 fibers, also featuring adequate amount of Li_2CO_3 to fully react with. It took 50 hours of dwell time at 650 °C for full lithiation, and this reaction proved particularly useful because of the finer microstructure and much higher flexural strength obtained. In the best case, it was indeed multiplied by 9 compared to the bare matrix.

Al powder was found to be a better option than Al_2O_3 fiber, as Al-reinforced matrices were mechanically superior and featured better porosity, which can translate to better performances in a MCFC cell.

Acknowledgments

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