

An investigation of shelf-life of strontium doped LaMnO₃ materials

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The shelf-life of Sr doped LaMnO₃ (LSM) materials of varying stoichiometric compositions prepared by wet chemical synthesis was investigated under storage conditions of low and high humidity at ambient temperature for ~350 days. It has been found that the adhesion, chemical stability and stability of the electrode performance of LSM materials are critically dependent on the A-site stoichiometry (i.e., (La + Sr)/Mn ratio) of the LSM materials and much less dependent on storage conditions (humidity level and storage time) over the period investigated. In this respect, LSM materials with stoichiometric and sub-stoichiometric compositions where (La + Sr)/Mn ≤ 1 are stable and LSM with A-site sub-stoichiometry ((La+Sr)/Mn ≤ ~0.9) is effective in achieving good adherence, high chemical stability and high stability of electrode performance. © 2000 Kluwer Academic Publishers

1. Introduction

Strontium doped LaMnO₃ (LSM) materials are the most common cathode materials for solid oxide fuel cells with Y₂O₃-ZrO₂ as electrolyte substrates. The thermal expansion, electrical and ionic conductivity properties [1–3], the oxygen diffusion coefficient [4, 5], the chemical stability with Y₂O₃-ZrO₂ electrolyte [6–8], the sintering behaviour [9, 10], and the electrochemical performance [11,12] of LSM materials have been extensively investigated. Despite the importance of LSM cathode materials in solid oxide fuel cells (SOFCs), the stability and shelf-life studies of LSM materials are rare. Bergsmark *et al.* [13] studied the stability of LSM powder with a small lanthanum excess (A-site over-stoichiometry) and found that the pellets prepared from the powder disintegrated after exposure to air, due to the formation of La(OH)₃. Stability of LSM powder decreased with increasing (La + Sr)/Mn ratio. However, it appears that a detailed investigation of the shelf-life and performance of LSM materials as a function of A-site stoichiometry has not been reported in the literature.

In this study, the effect of humidity and A-site stoichiometry on the shelf-life of LSM materials has been investigated. The shelf-life properties were characterised by the adhesion, the chemical stability with yttria-zirconia electrolytes and the electrochemical performance of LSM materials in the form of powder, ink

and as-fired coatings. The storage period was chosen to be about 1 year.

2. Experimental and materials

2.1. Powder preparation & storage conditions

LSM powders with two different stoichiometric compositions, (La_{0.8}Sr_{0.2})_{1.0}MnO₃ (A/B = 1, LSM-A) and (La_{0.8}Sr_{0.2})_{0.9}MnO₃ (A/B = 0.9, LSM-B), were targeted using a wet chemical synthesis method. Each LSM powder was divided into two batches and coarsened for 4 hrs in air at 900°C and 1000°C, respectively. The LSM compositions and coarsening conditions are given in Table I.

Inks were prepared from LSM powders and the electrode coatings were screen printed onto the electrolyte substrates, followed by sintering at 1150°C. The electrolyte substrates of 3 mol% Y₂O₃-ZrO₂ composition (TZ3Y, Tosoh, Japan) were prepared by tape casting, and were 20 mm in diameter and ~150 μm thick. The electrode coating area was ~0.44 cm². Pt paste (Engelhard 6082) was applied to the reverse side of the electrolyte disc to make counter and reference electrodes. The counter electrode was in the centre of the disc opposite the LSM electrode and the reference electrode was a ring around the counter electrode. Pt mesh was used as current collector. There were no significant

TABLE I Compositions and coarsening temperatures of starting LSM powders

LSM powder	Target composition	Coarsening conditions
LSM-A1	(La _{0.8} Sr _{0.2}) _{1.0} MnO ₃	900°C, 4 h, air
LSM-A2	(La _{0.8} Sr _{0.2}) _{1.0} MnO ₃	1000°C, 4 h, air
LSM-B1	(La _{0.8} Sr _{0.2}) _{0.9} MnO ₃	900°C, 4 h, air
LSM-B2	(La _{0.8} Sr _{0.2}) _{0.9} MnO ₃	1000°C, 4 h, air

differences in the surface quality of coatings prepared from LSM powders with different compositions and coarsening temperatures.

Three forms of LSM materials were chosen for the shelf-life study: LSM powder, LSM ink and as-fired LSM coating. Storage of LSM samples were carried out at ambient temperatures which varied between 15 to 28°C over the storage period. LSM inks were stored in airtight glass bottles while LSM powders and as-fired coatings were stored under two different humidity conditions. The first group of LSM powders and as-fired LSM coatings were stored in loosely closed glass bottles and placed in the normal laboratory conditions where humidity varied between 20 and 30% depending on the season and time (low humidity conditions). The second group of samples of LSM powders and as-fired coatings were also stored in loosely closed glass bottles and placed in a sealed dessicator in which the atmosphere was in equilibrium with a saturated KBr solution (high humidity conditions). The humidity of saturated KBr solution at 20°C is 84%. LSM powders in the bottles were stirred from time to time in order to even out the exposure to the environment.

2.2. Characterisation

X-ray diffraction (XRD) data of LSM powders, LSM inks and as-fired LSM coatings stored under both low and high humidity conditions at various times were collected with a Siemens 500 X-ray diffractometer, using Cu K_{α1} radiation. For XRD samples of LSM inks, the inks were heated slowly to 500°C for 5 hours in a pre-cleaned and fired alumina crucible to remove the media and water content. The electrode surface and electrode/electrolyte interface region were examined by scanning electron microscopy (SEM) before and after electrochemical testing. The chemical stability with TZ3Y electrolyte (the phase formation) was examined by X-ray energy dispersive spectrometry (EDS) and XRD.

The adhesion tests of the LSM coating to the electrolyte substrates were carried out by breaking the electrolyte from the middle of the coating. With good adhesion, the coating stuck very well to the TZ3Y electrolyte substrates and there was no delamination of the coatings after breaking the cell. With poorly adhered coatings, coatings peeled away from the substrate and could be easily removed after breaking the substrates.

The electrochemical performance of LSM coatings were evaluated under a cathodic current of 250 mA cm⁻² at 900°C in air by a galvanostatic current interruption (GCI) technique [14]. The initial polarisation performance was measured before passing any current and the stable polarisation performance was obtained after the electrodes were treated at a cathodic current density of 250 mA cm⁻² for 3 hours.

saturation performance was measured before passing any current and the stable polarisation performance was obtained after the electrodes were treated at a cathodic current density of 250 mA cm⁻² for 3 hours.

3. Results and discussion

3.1. Characterisation of LSM materials before storage

Fig. 1 is the XRD pattern of the initial LSM powders. For the LSM powders coarsened at 900°C, La₂O₃ was detected in the A-site sub-stoichiometric powder (LSM-B1) and La₂O₃ and La(OH)₃ were detected in the A-site stoichiometric powder (LSM-A1). On the other hand, for the LSM powders coarsened at 1000°C, the XRD patterns were ascribed to a single perovskite phase. The La₂O₃ and La(OH)₃ phases were not detected for either composition within the limit of the XRD technique. This indicates that coarsening at temperatures below 1000°C may not be sufficient to form a single perovskite phase for either LSM-A or LSM-B compositions for the wet chemical synthesis method used in this work.

Fig. 2 is the XRD pattern of the ink prepared from LSM-A and LSM-B powders coarsened both at 900°C and 1000°C. The ink samples were pre-heated at 500°C for 5 hrs. For LSM inks prepared from the powders coarsened at 900°C (LSM-A1 and LSM-B1), the existence of La₂O₃ was clearly visible. But the XRD peak intensities associated with La₂O₃ were much weaker than the corresponding powders. There is no change of the XRD pattern for the LSM inks prepared from

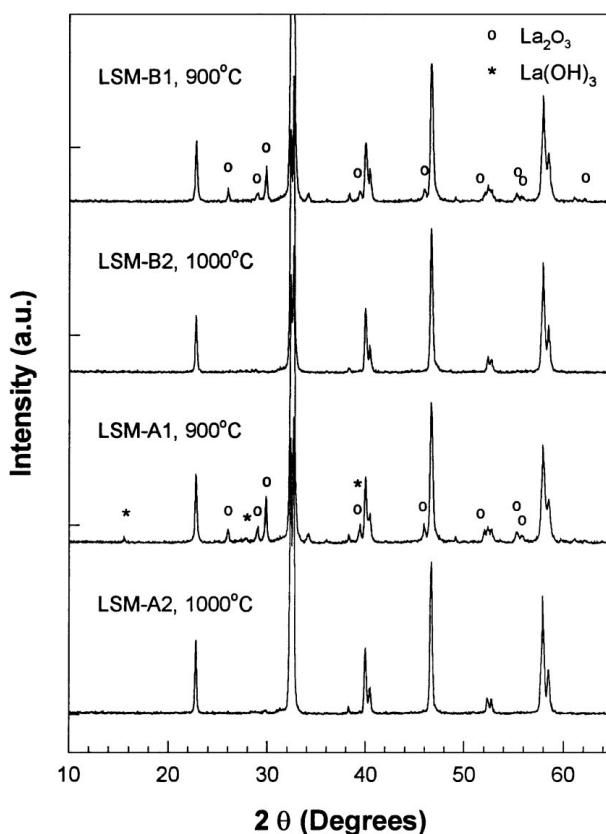


Figure 1 XRD patterns of starting LSM-A and LSM-B powders coarsened at 900°C and 1000°C.

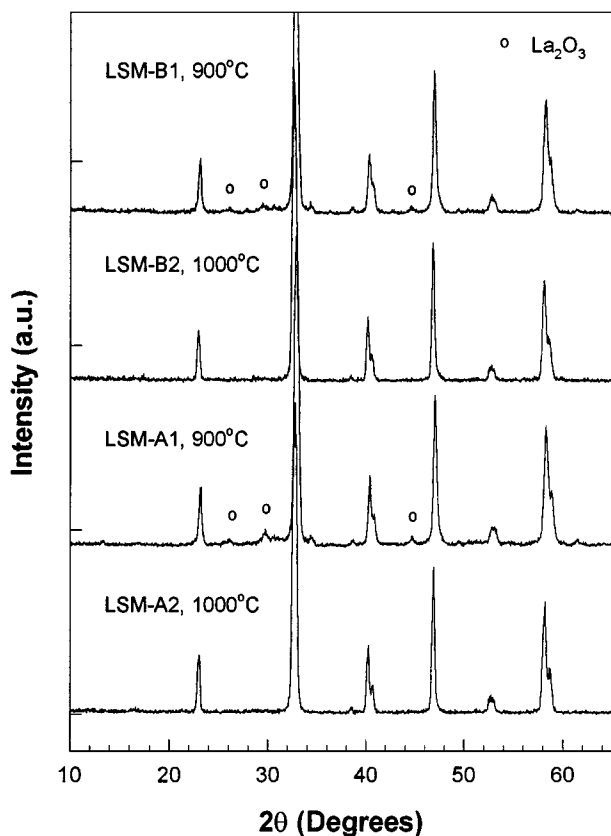


Figure 2 XRD patterns of the LSM inks prepared from starting powders of LSM-A and LSM-B compositions coarsened at 900°C and 1000°C.

powders coarsened at 1000°C (LSM-A2 and LSM-B2) as compared to the corresponding LSM powders.

The surface of as-fired LSM coatings on zirconia electrolyte prepared using different starting LSM powders were also examined by XRD. The XRD pattern basically showed the perovskite phase and zirconia phase. The peaks associated with La_2O_3 and $\text{La}(\text{OH})_3$ in the original LSM-A1 and LSM-B1 powders disappeared. Morphologies of the LSM electrode coatings before the fuel cell testing are shown in Fig. 3. The particle size is in the range of $\sim 0.7 \mu\text{m}$ for LSM-B1 and LSM-B2 and $\sim 0.4 \mu\text{m}$ for LSM-A1 and LSM-A2. The particle size of LSM-A was generally smaller than that of LSM-B. Nevertheless, the difference in the surface morphology and porous structure was very small between the coatings studied.

The adhesion of the coatings to TZ3Y electrolyte substrates was examined using the breaking test. For LSM coatings with A-site sub-stoichiometry (LSM-B1 and LSM-B2), the coatings adhered very well to the TZ3Y electrolyte substrate, with no signs of cracks or peeling after breaking the substrates. However, for LSM coatings with A-site stoichiometry (LSM-A1 and LSM-A2), the coatings spalled and were easily scratched from the YSZ substrate after breaking the substrates. The coatings of LSM-A1 and LSM-A2 were also found to have delaminated after electrochemical testing, whereas LSM-B1 and LSM-B2 coatings adhered very well to the TZ3Y electrolyte. The results

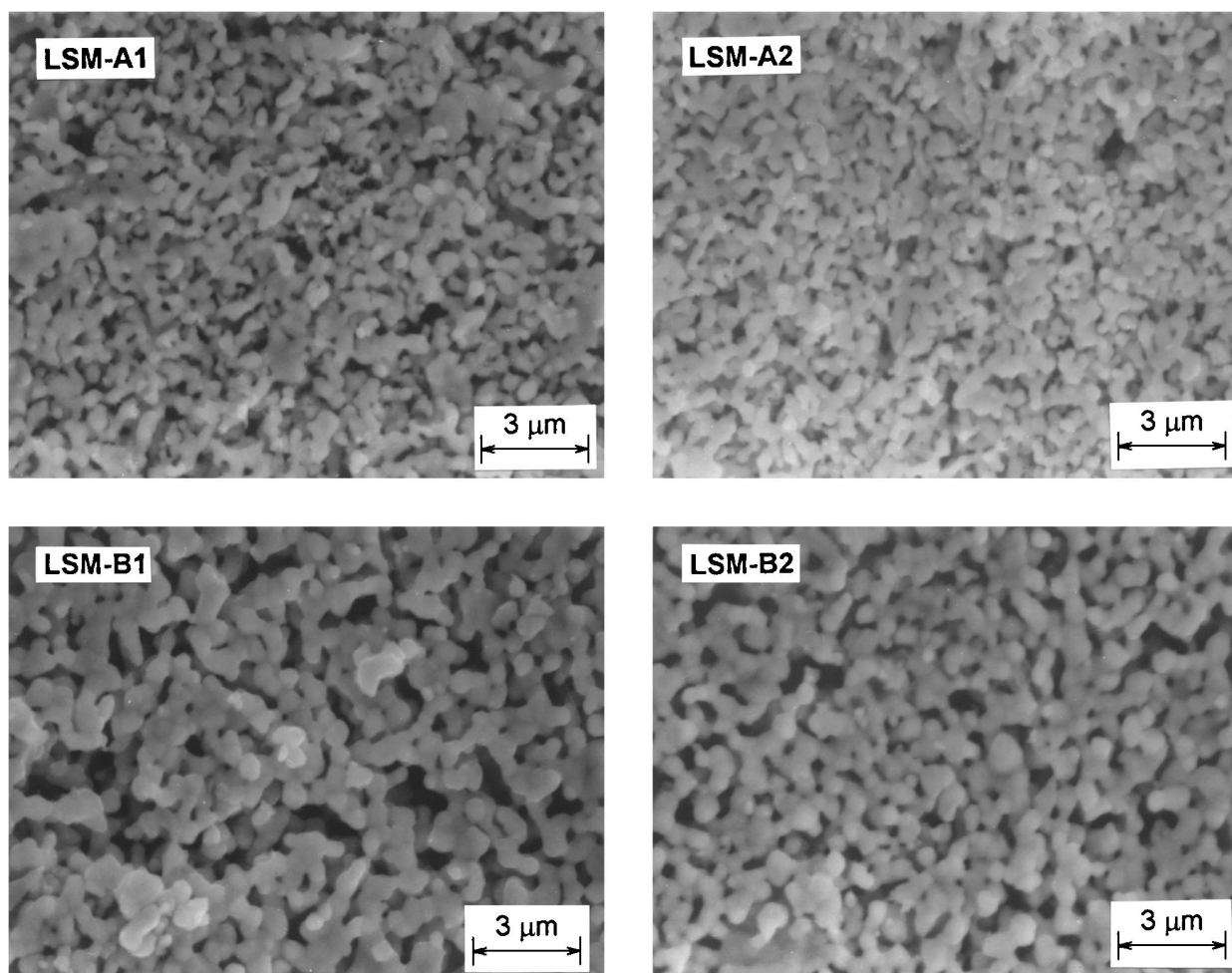


Figure 3 SEM pictures of the LSM electrode coatings before fuel cell testing.

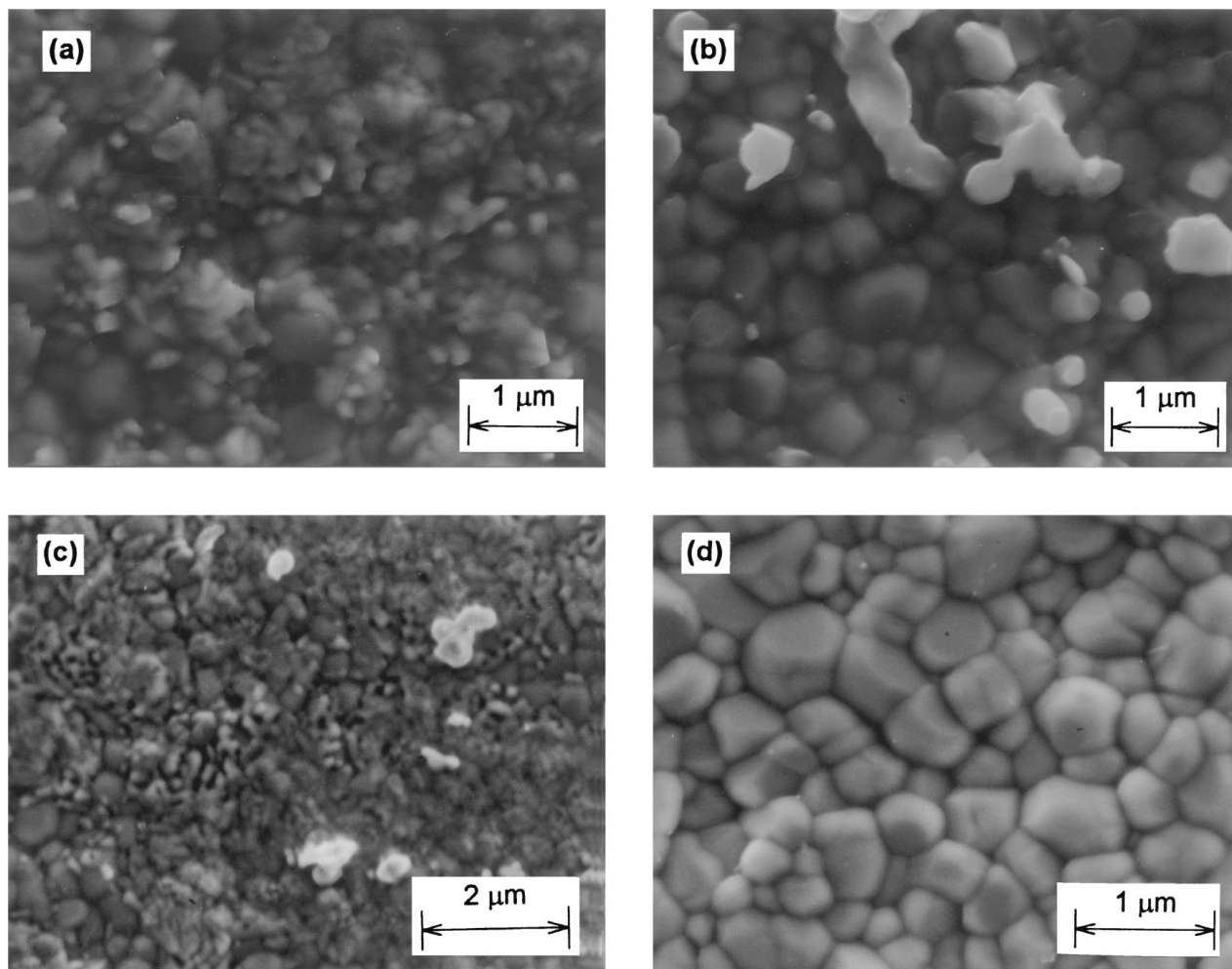


Figure 4 SEM pictures of the TZ3Y electrolyte surface after removal of (a) LSM-A2 and (b) LSM-B2 coatings before electrochemical testing, (c) LSM-A2 coating after cathodic current treatment, and (d) TZ3Y surface without any LSM coating contact.

clearly indicate that the adhesion properties of LSM electrode coatings were strongly affected by A-site stoichiometric composition but not affected by the coarsening temperature of the powder nor by the cathodic current treatment under the conditions used in this study.

Fig. 4 shows the SEM pictures of the TZ3Y electrolyte surface after removal of LSM-A2 (Fig. 4a) and LSM-B2 (Fig. 4b) coatings before the electrochemical testing. Fig. 4c shows the LSM-A2 coating after cathodic current passage of 250 mA cm^{-2} for 3 hours at 900°C . For comparison, the TZ3Y surface without being in contact with LSM coating is also shown in Fig. 4d. On the electrolyte surface in contact with the LSM-A2 coating, there was clearly a formation of fine particles ($\sim 0.1 \mu\text{m}$) in the vicinity of the grain boundaries on the TZ3Y surface. The fine particles were found to be La rich by EDS analysis and were identified by XRD to be the pyrochlore phase, $\text{La}_2\text{Zr}_2\text{O}_7$, as shown in Fig. 5. After current passage (polarisation) of 250 mA cm^{-2} for 3 hours at 900°C , the LSM-A2 coating delaminated and the fine particles of lanthanum zirconate were still clearly visible. This indicates that the lanthanum zirconate formed during electrode firing (1150°C , 4 hours) did not decompose by the cathodic current treatment conditions used here. On the other hand, the morphology of the TZ3Y electrolyte surface after being in contact with the LSM-B2 coating was

very similar to that of a clean TZ3Y surface (Fig. 4d). Neither XRD nor EDS could detect any lanthanum or strontium zirconate phases on the TZ3Y surface. The bright-contrast particles were identified as LSM particles remaining on the TZ3Y surface after removal of the coating with a scalpel. The formation of the lanthanum zirconate phase for LSM powder with the LSM-A composition in the present study is generally in agreement with those reported in the literature [15, 16].

The initial and stable polarisation performance of LSM coatings were measured before and after treatment of a cathodic current density of 250 mA cm^{-2} for 3 hours at 900°C . The results are summarised in Table II. For the LSM-A1 and LSM-A2 electrodes, the overpotential losses were very high and there was a

TABLE II The overpotential losses (η) measured at 250 mA cm^{-2} and 900°C before and after cathodic current treatment (250 mA cm^{-2} , 3 hrs). LSM electrodes were prepared from the powders before the storage

LSM Electrode	η , mV	
	Before current treatment	After current treatment
LSM-A1 ^a	309 ± 87	107 ± 69
LSM-A2 ^a	279 ± 104	130 ± 18
LSM-B1	164	93
LSM-B2	134 ± 40	52 ± 7

^aElectrode coatings delaminated after electrochemical evaluation.

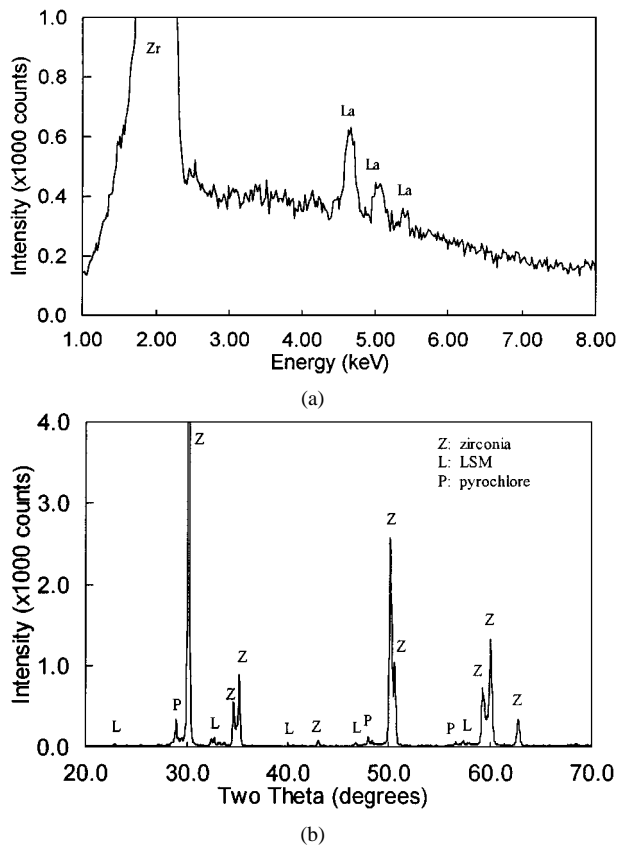


Figure 5 (a) EDS and (b) XRD pattern of the TZ3Y electrolyte surface following removal of LSM-A2 coating as shown in Fig. 4a.

much wider scatter in the initial η values (no current passage) in comparison with LSM-B1 and LSM-B2 electrodes. It was found that the electrode resistances measured between the LSM electrode and reference electrode were also significantly higher for LSM-A1 and LSM-A2 electrodes than that of the LSM-B1 and LSM-B2 electrodes. After the cathodic current treatment of 250 mAcm^{-2} , the overpotential losses of all LSM electrodes studied were significantly reduced. However, for the LSM-A1 and LSM-A2 electrodes, the polarisation performance was not stable and the coatings were found to have delaminated after testing. This is most likely related to the poor adhesion and the formation of lanthanum zirconate phases in the case of LSM electrodes with A-site stoichiometry composition (LSM-A). In contrast, for LSM electrodes with A-site sub-stoichiometry (LSM-B), both overpotential losses and variation in polarisation performance were significantly reduced. The effect of cathodic current treatment on the polarisation performance is most likely associated with a change of surface composition of LSM near the electrode/electrolyte interface under oxygen reduction conditions [17].

3.2. Characterisation of LSM materials at the end of storage period

For all the LSM powders stored under low and high humidity conditions, there were no signs of white spots appearing as observed for the LSM pellets prepared from LSM with A-site over-stoichiometry composition [13]. During the storage period, small portions of

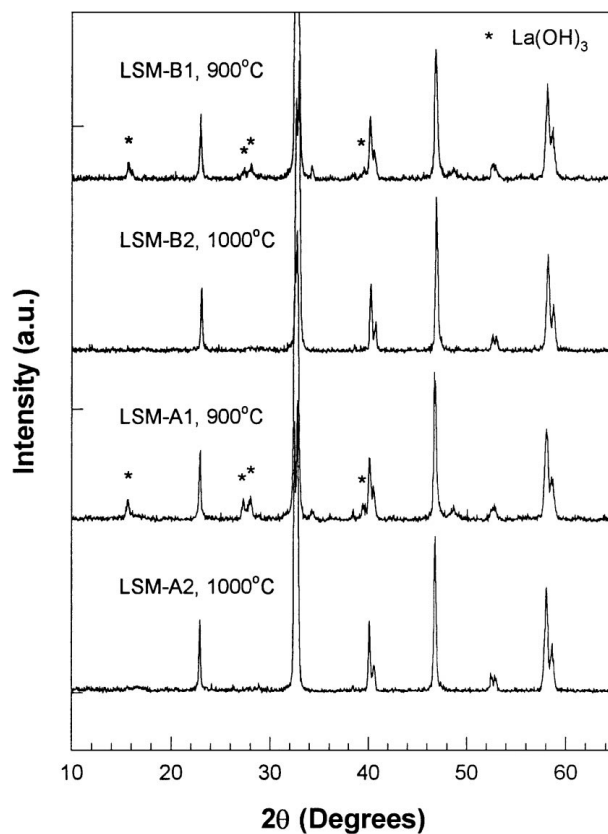


Figure 6 XRD patterns of the LSM powders stored under low humidity conditions for ~ 350 days at ambient temperatures.

powder samples were taken from the bottles and examined by XRD from time to time. However, there was no progressive change which could be identified from the XRD patterns of the powders. For example, the XRD patterns taken after 20 days storage were the same as those stored for 50 days and for ~ 350 days. Therefore, only the XRD pattern of the LSM powders at the end of the storage period were presented, as shown in Fig. 6 for the LSM powders stored under low humidity conditions for ~ 350 days. XRD patterns for LSM powders stored under high humidity conditions for ~ 350 days were almost the same as that shown in Fig. 6.

For the LSM powders coarsened at 900°C (LSM-A1 and LSM-B1), the La_2O_3 phase originally existing in the starting powder was completely converted to $\text{La}(\text{OH})_3$ under both low and high humidity conditions. This is indicated by the disappearance of XRD lines associated with La_2O_3 phase and the appearance and the increased intensity of XRD lines associated with $\text{La}(\text{OH})_3$. In the case of LSM powders coarsened at 1000°C (LSM-A2 and LSM-B2), the XRD patterns of the LSM powders were essentially the same as the starting powders, irrespective of the storage humidity level conditions. The XRD data of LSM inks stored in airtight bottles for ~ 350 days were also essentially the same as those of inks prepared from starting LSM powders. The only visible change of LSM inks was the increase in the ink viscosity. However, this can be adjusted by adding more media.

LSM inks were prepared from the LSM powders which had been stored under low and high humidity conditions for ~ 350 days and then LSM electrodes

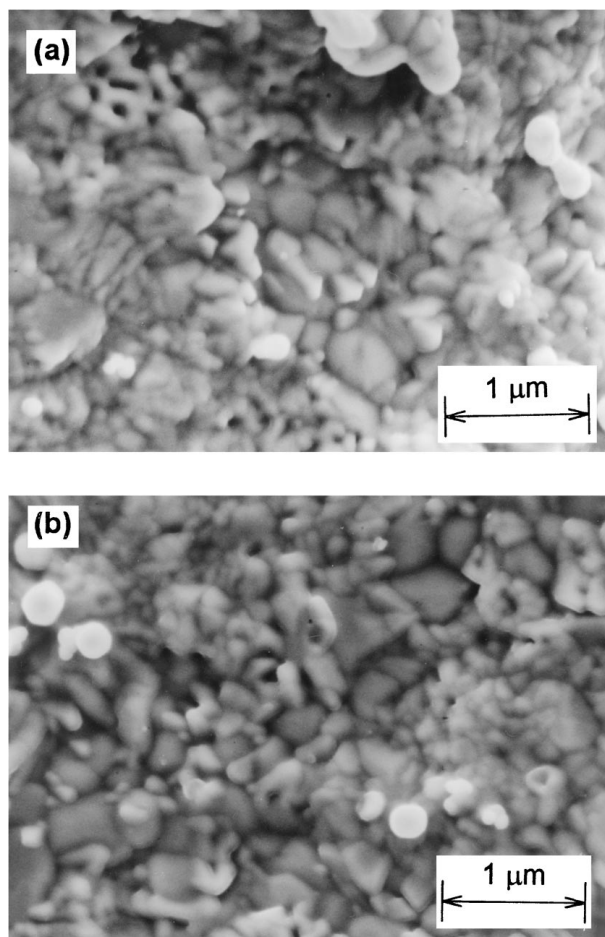


Figure 7 SEM pictures of the TZ3Y electrolyte surface following removal of (a) LSM-A1 and (b) LSM-A2 coatings before electrochemical testing. The coatings were prepared from inks stored for ~ 350 days.

were prepared. LSM electrodes were also prepared from LSM inks stored for ~ 350 days (old ink). The coatings were fired at 1150°C for 4 hours in air. Adhesion tests were carried out on all electrode coatings (including coatings stored for ~ 350 days under low and high humidity conditions) and the test results can be classified into two groups. The first group is the electrode coatings prepared from LSM-A compositions. Regardless of the powder coarsening temperature and the coating, ink or powder storage conditions, all electrode coatings of LSM-A compositions peeled off and delaminated after breaking the electrodes, just like that observed on the LSM-A coatings prepared from starting LSM powders. In contrast to the LSM-A coatings, all LSM electrodes prepared from LSM-B compositions adhered very well to the TZ3Y substrates after the breaking tests. The distinct behaviour of the adhesion properties of LSM-A and LSM-B coatings was also observed for the electrode coatings after electrochemical testing. The results clearly indicate that the adhesion properties of LSM electrode coatings are critically related to the A-site stoichiometry and not to the storage conditions of the powder in the LSM composition range studied here.

The electrode/electrolyte interface was examined for LSM-A1 and LSM-A2 electrodes prepared from inks stored for ~ 350 days. Fig. 7 shows the SEM pictures of the TZ3Y electrolyte surface following removal of

TABLE III Average of the overpotential losses of LSM electrodes measured at 250 mAcm^{-2} , 900°C before and after cathodic current treatment (250 mAcm^{-2} , 3 hrs). The electrodes were prepared from LSM inks and powders stored under low and high humidity conditions for ~ 350 days. The results were grouped based on compositions

LSM Electrode	η , mV	
	Before current treatment	After current treatment
LSM-A1 ^a	243 ± 67	167 ± 83
LSM-A2 ^a	424 ± 86	263 ± 117
LSM-B1	102 ± 27	32 ± 10
LSM-B2	123 ± 26	35 ± 17

^aElectrode coatings delaminated after electrochemical evaluation.

LSM-A1 and LSM-A2 coatings before electrochemical testing. On the TZ3Y electrolyte surface, the formation of fine particles on the electrolyte surface was clearly visible. The fine particles were identified by EDS/XRD to be pyrochlore phase, $\text{La}_2\text{Zr}_2\text{O}_7$, the same as that shown in Fig. 5.

The overpotential losses of LSM electrodes prepared from inks and powders stored for ~ 350 days were measured before and after treatment with a current density of 250 mAcm^{-2} for 3 hours at 900°C . It was found that the stability and reproducibility of electrochemical performance of the LSM electrodes were predominantly dependent on the A-site stoichiometry and not on the storage conditions or the storage period of LSM inks and powders. Thus, for clarity, the overpotential losses were grouped based on composition and coarsening temperatures of the LSM powders, as shown in Table III. The electrochemical performance of electrode coatings stored under low and high humidity conditions for ~ 350 days have similar overpotential ranges (see Table II) for the same compositions. Comparing the results in Tables II and III, it is clear that the reliability and stability of polarisation performance of LSM electrodes is critically dependent on the A-site stoichiometry composition and much less dependent on the storage conditions such as the humidity and the storage period under the conditions studied.

4. Summary and conclusions

The shelf-life of LSM materials of powder, ink and as-fired coating was investigated under storage conditions of varying humidity conditions for ~ 350 days. The shelf-life properties of LSM materials were measured by adhesion, chemical stability and stability of the electrochemical performance. From the results of these investigations, the following useful points are summarised.

1. Adhesion, chemical stability and stability of electrochemical performance of LSM electrodes with TZ3Y as electrolyte are strongly dependent on the A-site stoichiometry (i.e., the $(\text{La} + \text{Sr})/\text{Mn}$ ratio) of the LSM powder. There is essentially no change in the adhesion, chemical and electrochemical properties of LSM electrodes prepared from old inks or from inks prepared from LSM powder stored under low and high humidity conditions for ~ 350 days.

Therefore, unlike over-stoichiometric LSM materials [13], LSM materials with A-site stoichiometric and sub-stoichiometric compositions are stable under the humidity range of 20 to 84% at ambient temperatures over the period studied. An A-site sub-stoichiometry where $(\text{La} + \text{Sr})/\text{Mn} = \sim 0.9$ is effective of inhibiting the formation of lanthanum zirconate and achieving good adhesion, high chemical stability and stable electrochemical performance.

2. The change found for LSM powders stored under high humidity conditions is the same as that found for the powder stored under low humidity conditions, i.e., complete transfer of un-reacted lanthanum oxide into lanthanum hydroxide. However, the results clearly demonstrated that the presence of La_2O_3 and $\text{La}(\text{OH})_3$ peaks in XRD patterns does not necessarily indicate poor adhesion and unstable electrochemical performance of these LSM powders as shown by LSM-B coarsened at 900°C . Coarsening LSM powder at 900°C or 1000°C has no effect on the shelf-life properties of LSM materials.

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