# Precipitation behavior of highly Sr-doped LaPO<sub>4</sub> in phosphoric acid solutions

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The precipitation condition of  $LaPO_4$  in phosphoric acid solution was investigated under both atmospheric and humidified conditions. The crystal morphology, Sr doping level,  $H_2O$  incorporation, and high temperature stability of Sr-doped LaPO<sub>4</sub> precipitates were also analyzed.

- Increasing  $pH_2O$  from 0.01 to 1 atm extends the precipitation region of LaPO<sub>4</sub> in phosphoric acid solutions toward higher temperatures by nearly 100 °C. Under such conditions (*e.g.* T = 250 °C and  $pH_2O = 1$  atm), it is possible to obtain aggregated crystals up to 200 µm. The Sr doping level in LaPO<sub>4</sub> shows a strong dependence on the precipitation ratio of La,  $X_{La}$ . The Sr doping level is higher in the low  $X_{La}$  region, reaching 20 mol% at maximum. This value is one order of magnitude
- <sup>15</sup> higher than the previously reported solubilities. It was confirmed  $H_2O$  is certainly incorporated in the bulk by Sr doping. The solubility of Sr in LaPO<sub>4</sub> would be sufficiently high (at least 20.1 %) even at 600 °C; however, it becomes considerably lower at 1200 °C.

### 1. Introduction

In recent years, lanthanum orthophosphate (LaPO<sub>4</sub>) has <sup>20</sup> received attention because of its potential application as a solid electrolyte in fuel cells.<sup>1-4</sup> It exhibits protonic conductivity on the order of  $10^{-4}$  S cm<sup>-1</sup> at 700 °C when La is partially substituted with alkaline earth metals such as Sr.<sup>1,5</sup> For practical use, however, further enhancement of the <sup>25</sup> conductivity is necessary.

Amezawa *et al.* reported that the conductivity of Sr-doped LaPO<sub>4</sub> increased with increasing the dopant concentration.<sup>6</sup> They also reported that the solubility of Sr in LaPO<sub>4</sub>, represented by the molar ratio Sr/(La+Sr), was approximately

- $_{30} 2 \%$ .<sup>7</sup> With higher Sr mixing ratios, a secondary phase, Sr<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, appeared and the conductivity decreased with increasing Sr concentration. Thus, the low solubility of Sr is an obstacle to enhancing the conductivity of LaPO<sub>4</sub>.
- While the solubility research described above was <sup>35</sup> conducted with samples prepared by solid state reaction and sintered at 1200 °C,<sup>7</sup> there are several reports of different Sr doping levels with different synthesis temperatures. Tyholdt *et al.* reported the solubility of Sr in LaPO<sub>4</sub> to be ~1 % with samples sintered at 1450 °C.<sup>8</sup> Gallini *et al.* prepared 5 % Sr-
- <sup>40</sup> doped LaPO<sub>4</sub> by combustion synthesis followed by calcination at 800 °C.<sup>3</sup> Schatzmann *et al.* synthesized Sr-doped LaPO<sub>4</sub> by adding La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Sr(NO<sub>3</sub>)<sub>2</sub> to heated phosphoric acid at 150 °C, followed by precipitation of LaPO<sub>4</sub> within 30 minutes.<sup>9</sup> With this method, at least 4 % Sr-doped LaPO<sub>4</sub> was
- <sup>45</sup> obtained. These results suggest that the solubility of Sr would be higher at lower temperatures. Besides temperature, water vapor pressure may also affect the solubility of Sr. When Sr is doped into LaPO<sub>4</sub>, a certain amount of water is also introduced into LaPO<sub>4</sub> as represented by the following <sup>50</sup> expression:

$$(1-x) LaPO_4 + (x/2) Sr_2P_2O_7 + (y/2) H_2O \rightarrow La_{1-x}Sr_xH_yPO_{4-(y/2)+(y/2)}.$$
 (1)

Therefore, Sr-doped LaPO<sub>4</sub> (La<sub>1-x</sub>Sr<sub>x</sub>H<sub>y</sub>PO<sub>4-(x/2)+(y/2)</sub>) would be stabilized with higher water vapor pressure. However, the relationship between the solubility of Sr and these parameters <sup>55</sup> has not been clarified yet.

When the above synthesis methods are used, powder samples are generally obtained. For use as electrolytes, they need to be sintered at over 1000 °C for densification. This heat treatment is expected to limit the solubility of Sr to <sup>60</sup> approximately 2 %. <sup>7</sup> Therefore, to synthesize highly Sr-doped LaPO<sub>4</sub>, avoiding high temperature heat treatments in syntheses would also be important.

Synthesis of single crystals of rare earth ultraphosphates (REP<sub>5</sub>O<sub>14</sub>, RE: rare earth elements) in phosphoric acid <sup>65</sup> solutions has been the subject of intensive investigations since the 1970s, for the purpose of using them as laser materials. <sup>10,11</sup> In the series of these researches, Chudinova *et al.* investigated the La<sub>2</sub>O<sub>3</sub> – P<sub>2</sub>O<sub>5</sub> – H<sub>2</sub>O system and reported that LaPO<sub>4</sub> precipitated in phosphoric acid solutions at below <sup>70</sup> 160 °C. <sup>12</sup> Although there is no detailed information on the precipitation behavior of LaPO<sub>4</sub>, it is possible to obtain Sr-doped LaPO<sub>4</sub> with sufficiently large size and density for use as electrolytes directly.

Therefore, synthesis of LaPO<sub>4</sub> in homogeneous phosphoric <sup>75</sup> acid solutions was performed in this research. The conditions (temperature and water vapor pressure) where LaPO<sub>4</sub> can be precipitated in phosphoric acid solutions were investigated. The morphology of precipitates was also observed. Then, the condition dependence of the Sr doping level was analyzed to <sup>80</sup> reveal the optimum condition for obtaining highly Sr-doped LaPO<sub>4</sub>. The effectiveness of Sr doping was verified by observing unit cell volume changes by doping and the evaporation of H<sub>2</sub>O which had been incorporated into LaPO<sub>4</sub> during the synthesis. Finally, the stability of Sr-doped LaPO<sub>4</sub> at high temperatures was investigated.

### 2. Experimental

### 2.1. Synthesis

- $_5$  Undoped and Sr-doped LaPO<sub>4</sub> were synthesized by precipitation in homogeneous phosphoric acid solutions containing La<sub>2</sub>O<sub>3</sub> and SrCO<sub>3</sub>. La<sub>2</sub>O<sub>3</sub> (99.99%, Nacalai Tesque), SrCO<sub>3</sub> (99.99%, Wako Pure Chemical Industries), and H<sub>3</sub>PO<sub>4</sub> (85%, Nacalai Tesque) were mixed in a perfluoroalkoxy 10 (PFA) beaker and held at 190 °C in a furnace for several days
- to obtain a transparent solution. Then temperature and water vapor pressure were changed and held for a predetermined period of time to precipitate LaPO<sub>4</sub>. The temperature was set between 120 °C and 250 °C, and the water vapor pressure was 15 set to approximately 0.01 atm (atmospheric conditions) or 1
- atm (humidified conditions). Synthesis parameters are summarized in Table 1 and Table 2.

For humidification, the apparatus shown in Fig. 1 was used. The whole apparatus was placed in a furnace kept at a 20 constant temperature. A beaker was put on a stainless steel floor plate and covered with a stainless steel box with a capacity of 2.64 L. A 4-m-long spiral tube was attached to a side wall of the box. Liquid water was fed to the box through the spiral tube so that it evaporated before reaching the box.

25 The liquid water feed rate was 0.1 mL/min, which was equivalent to 0.18 L-H<sub>2</sub>O(g)/min at 120 °C and 0.24 L- $H_2O(g)/min$  at 250 °C. The apparatus was not sealed tightly so that the inner gas was able to flow out through the narrow gap between the box and the floor plate when the inner pressure 30 exceeded 1 atm. Therefore, the water vapor pressure inside the

box was expected to be 1 atm.

After the predetermined precipitation period, the beaker was cooled down to room temperature. In general, there were precipitates on the bottom of the beaker and the transparent

35 solution above them. The solution was collected for the chemical analysis. The precipitates were washed well with hot water (~90 °C).

### 2.2. Characterization

- Phase identification was carried out via X-ray powder 40 diffraction (XRD) analysis on PANalytical X'Pert-Pro MPD using Cu Ka radiation at room temperature. The unit cell volume of samples was evaluated by the Rietveld method using X'Pert HighScore Plus (Version 2.2c) software. The morphology of precipitates was investigated using KEYENCE
- 45 VE-7800 scanning electron microscopy (SEM). Chemical analysis of solutions and precipitates was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on Seiko Instruments SPS4000.

The amount of H<sub>2</sub>O evaporated from samples was 50 determined by the Karl Fischer titration method. The samples were dried in advance at 600 °C for 50 h in the air ( $pH_2O \sim$ 0.01 atm) to eliminate residual water and phosphoric acid on the surface of samples. The protons responsible for the proton conduction were still expected to remain in the samples,

55 judging from the reported pH2O dependence of the

conductivity at 600 °C. <sup>6</sup> Then each sample was held at 800 °C under dry nitrogen flow (200 mL/min) to be dehydrated. The nitrogen which contains the released H<sub>2</sub>O was transferred to the Karl Fischer moisture titrator to 60 determine the amount of H<sub>2</sub>O evaporated from the sample. For this, Kyoto Electronics Manufacturing MKC-510N (Karl-Fischer moisture titrator) and ADP-512S (evaporator) were utilized.

Table 1 Initial co	ompositions	of solutions	for the s	synthesis o	f LaPO₄.
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	Starting materials	Initial composition			
Abbrev.		Molar ratio La : Sr : P	$\left(\frac{Sr}{La+Sr}\right)$ (mol%)		
Sr0		1.00 : 0.00 : 15	0		
Sr4	La <sub>2</sub> O <sub>3</sub> , SrCO <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub>	0.96 : 0.04 : 15	4		
Sr8		0.92:0.08:15	8		

Table 2 Dissolution and precipitation conditions for the synthesis of LaPO<sub>4</sub>.

Abbrev.	Dissolution		Precipitation		
	Temp. (°C)	pH <sub>2</sub> O (atm)	Temp. (°C)	pH <sub>2</sub> O (atm)	
A230 A140 A120 H250 H140 H120	190	~0.01	230 140 120 230 140 120	~0.01 ~0.01 ~1 ~1 ~1 ~1	



70 Fig. 1 Schematic illustration of the apparatus used for humidification during the precipitation of LaPO<sub>4</sub>.

#### 3. **Results and discussion**

### 3.1. Precipitation condition and crystal morphology of LaPO<sub>4</sub> and LaP<sub>3</sub>O<sub>9</sub>

75 The precipitation condition of LaPO<sub>4</sub> was investigated using solutions with the composition Sr0. Experiments were performed under both atmospheric (A230, A140) and humidified (H250, H140) conditions. Fig. 2 shows the X-ray diffraction patterns of the precipitates obtained under each <sup>80</sup> condition. Under the atmospheric conditions, monazite-type LaPO<sub>4</sub> was obtained at 140 °C while LaP<sub>3</sub>O<sub>9</sub> was obtained at 230 °C. This is consistent with the results reported by



Fig. 2 X-ray powder diffraction patterns of undoped  $LaPO_4$  and  $LaP_3O_9$  precipitates obtained under the conditions (a) A230, (b) A140, (c) H250, and (d) H140.

- <sup>5</sup> Chudinova *et al.* <sup>12</sup> Under the humidified conditions, monazite-type LaPO<sub>4</sub> was obtained both at 250 °C and 140 °C. With these results, the precipitation region of LaPO<sub>4</sub> was drawn on the temperature –  $pH_2O$  plane (Fig. 3). As indicated in the figure, increasing  $pH_2O$  from 0.01 to 1 atm extends the
- <sup>10</sup> precipitation region of LaPO<sub>4</sub> toward higher temperatures by nearly 100 °C. At 1 atm H<sub>2</sub>O, LaPO<sub>4</sub> can be obtained even at 250 °C, where LaP<sub>3</sub>O<sub>9</sub> will be obtained at lower pH<sub>2</sub>O such as 0.2 atm. The analogous phenomenon for LaP<sub>3</sub>O<sub>9</sub> and LaP<sub>5</sub>O<sub>14</sub> was reported in detail by Balagina *et al.* <sup>13</sup>
- <sup>15</sup> Fig. 4 shows SEM images of undoped LaPO<sub>4</sub> and LaP<sub>3</sub>O<sub>9</sub> precipitates. Under the conditions A140 and H140, LaPO<sub>4</sub> precipitates were rice-shaped particles with a size range of 500 nm  $1 \mu$ m. In contrast, under H250 condition, the LaPO<sub>4</sub> precipitates were dense aggregates of well-shaped crystals up
- $_{20}$  to 200 µm. Thus, the precipitation temperature had a marked effect on the crystal growth of LaPO<sub>4</sub>. Higher precipitation temperatures, in combination with humidification, may enable direct syntheses of dense LaPO<sub>4</sub> electrolytes in phosphoric acid solutions.



Fig. 4 SEM images of undoped  $LaPO_4$  and  $LaP_3O_9$  precipitates obtained under the conditions (a) A230, (b) A140, (c) H250, and (d) H140.

## 3.2. Optimum condition for obtaining highly Sr-doped LaPO<sub>4</sub>

<sup>30</sup> Attempts to synthesize Sr-doped LaPO<sub>4</sub> were carried out using solutions with the compositions Sr4 and Sr8. Experiments were performed in the precipitation region of LaPO<sub>4</sub> (see Fig. 3) under both atmospheric (A120) and humidified (H250, H120) conditions. The precipitation period was varied to <sup>35</sup> observe changes in the composition of precipitates and solutions with time. In each condition, single phase LaPO<sub>4</sub> was precipitated, as confirmed by X-ray diffraction.

Fig. 5 shows the change in the composition of the solutions with time measured by ICP. The concentrations of La and Sr <sup>40</sup> decreased with time. In particular, under H120 condition, the concentrations decreased rapidly by 2 – 3 orders. This indicates that the solubility of LaPO<sub>4</sub> in phosphoric acid solutions is especially low under H120 condition, or the driving force for the precipitation is strong under that <sup>45</sup> condition. This result corresponds well to the fact that H120 condition is quite deep in the precipitation region of LaPO<sub>4</sub> in Fig. 3. Under A120 condition, the changes in the



SolidThisRef.Ref.phasework1213LaP\_5O\_{14} $\diamondsuit$ LaP\_3O\_9 $\boxplus$  $\clubsuit$ LaPO\_4 $\blacktriangle$ None $\boxtimes$ 

<sup>50</sup> Fig. 3 Phase stability diagram of the  $La_2O_3 - P_2O_5 - H_2O$  system with a constant La/P ratio (La : P = 1 : 15). In addition to the results obtained in this study, previous results reported by Chudinova *et al.*<sup>12</sup> and Balagina *et al.*<sup>13</sup> are also shown.



Fig. 5 Change in composition of solutions with time under the conditions (a) A120, (b) H250, and (c) H120. Inset in (c) is a logarithmic plot.

concentrations of La and Sr fluctuated. This is likely due to the fluctuation of water vapor pressure in the atmosphere.

<sup>5</sup> For better understanding of the precipitation behavior, these concentration values were converted into "precipitation ratios." We defined the precipitation ratio of element M,  $X_{\rm M}$ , by the following formula:

$$X_{\rm M} \equiv \frac{n_{\rm M, \, prec}}{n_{\rm M, \, init}} \times 100 \ (\%), \tag{2}$$

- <sup>10</sup> where  $n_{\rm M, prec}$  and  $n_{\rm M, init}$  are the quantities of M in the precipitate and initial solution, respectively. For example,  $X_{\rm La}$  will be 100 % when all La in the initial solution precipitates as LaPO<sub>4</sub>. Fig. 6 shows the changes in  $X_{\rm La}$  and  $X_{\rm Sr}$ .  $X_{\rm Sr}$  was greater than  $X_{\rm La}$  in the early stages of the precipitation
- <sup>15</sup> regardless of the initial composition of the solution. This suggests the formation of Sr-richer LaPO<sub>4</sub> than the initial solutions.

The Sr doping levels in the LaPO<sub>4</sub> precipitates analyzed by ICP, Fig. 7, showed a strong dependence on  $X_{La}$ . In good



**Fig. 6** Change in the precipitation ratios of La and Sr observed along with the progression of the precipitation of LaPO<sub>4</sub>.

agreement with the precipitation ratio changes described above (Fig. 6), the Sr doping levels in the precipitates were <sup>25</sup> higher in the low  $X_{La}$  region, reaching 20 mol% at maximum. This value is one order of magnitude higher than the reported solubilities of Sr in LaPO<sub>4</sub>. <sup>7,8</sup> The precipitation temperature and  $pH_2O$  did not seem to have a significant effect on this trend, although they affect the attainable precipitation ratio <sup>30</sup> limited by thermodynamics, and the Sr doping level accordingly. Thus, it can be concluded that the precipitation method in homogeneous phosphoric acid solutions serves as the most effective synthesis route to date for highly Sr-doped LaPO<sub>4</sub>.

### 35 3.3. Effectiveness of Sr doping

To examine whether Sr was doped correctly and H<sub>2</sub>O was incorporated in the bulk as desired, the following two methods were used: (1) The amount of H<sub>2</sub>O evaporated from samples at 800 °C in dry N<sub>2</sub> was measured by the Karl Fischer titration <sup>40</sup> method. (2) The unit cell volume of samples was evaluated before and after the H<sub>2</sub>O evaporation measurement using



Fig. 7 Dependence of the Sr doping level in  $\mathrm{LaPO}_4$  on the precipitation ratio of La.

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Fig. 8 (a) H<sub>2</sub>O evaporation from Sr-doped LaPO<sub>4</sub> under N<sub>2</sub> at 800 °C as measured by the Karl Fischer titration (KFT) method. The samples were held in the air at 600 °C for 50 h beforehand. (b) Unit cell volume of Sr-5 doped LaPO<sub>4</sub> as determined by Rietveld analysis using powder X-ray diffraction patterns. The open circles ( $\bigcirc$ ) represent the cell volume of samples before the titration (just after held in the air at 600 °C for 50 h). The filled squares ( $\blacksquare$ ) represent the cell volume of samples after the titration.

<sup>10</sup> powder X-ray diffraction patterns. Prior to these measurements, samples were dried at 600 °C in the air for 50 h.

Fig. 8 (a) represents the  $H_2O$  evaporation from LaPO<sub>4</sub> (expressed in percentage of the initial weight of each sample) <sup>15</sup> with different Sr doping levels (0, 4, 8 and 18 mol%). Although the plots are not linear,  $H_2O$  evaporation monotonically increased with increasing the Sr doping level. This should indicate that  $H_2O$  was incorporated in LaPO<sub>4</sub> with Sr on the synthesis. Fig. 8 (b) shows the unit cell volume of

 $_{\rm 20}$  samples before and after the  $\rm H_2O$  evaporation measurement. In both cases,  $\rm LaPO_4$  with higher Sr doping level had larger

unit cell volume. This would indicate that Sr substituted for La in the monazite structure, since the ionic radius of  $Sr^{2+}$  in ninefold coordination (1.31 Å) is larger than that of  $La^{3+}$  (1.21 <sup>25</sup> Å). <sup>14</sup> After the H<sub>2</sub>O evaporation measurement, the unit cell volume of Sr-doped LaPO<sub>4</sub> significantly decreased while that of undoped LaPO<sub>4</sub> remain unchanged. This would reflect the evaporation of H<sub>2</sub>O from the bulk Sr-doped LaPO<sub>4</sub>. In Fig. 8 (a) the small H<sub>2</sub>O evaporation was observed even from <sup>30</sup> undoped LaPO<sub>4</sub>, but it could be due to some residual water on the surface or grain boundaries of the sample.

These results suggest that Sr successfully substituted for La and H<sub>2</sub>O was certainly incorporated in the bulk as desired.

### 3.4. High temperature stability of Sr-doped LaPO<sub>4</sub>

35 To evaluate the stability of highly Sr-doped LaPO<sub>4</sub>, 13.4 % Sr-doped LaPO<sub>4</sub> and 20.1 % Sr-doped LaPO<sub>4</sub> synthesized in phosphoric acid solutions were heat treated at higher temperatures. The samples were first held at 600 °C for 80 h in the atmosphere, then the 13.4% doped sample was 40 additionally held at 1200 °C for 5 h. Fig. 9 shows the X-ray diffraction patterns obtained after each heat treatment. While no secondary phase was detected after the first heat treatment at 600 °C, the presence of secondary phases,  $Sr_2P_2O_7$  and  $Sr_3La(PO_4)_3$ , was clearly detected after the second heat <sup>45</sup> treatment at 1200 °C. Amezawa *et al.* reported Sr<sub>2</sub>P<sub>2</sub>O<sub>7</sub> as the secondary phase at 1200 °C and Sr<sub>3</sub>La(PO<sub>4</sub>)<sub>3</sub> at above 1350 °C. <sup>6</sup> Tyholdt *et al.* also reported both as the secondary phases at 1450 °C. <sup>8</sup> The detection of both  $Sr_2P_2O_7$  and  $Sr_3La(PO_4)_3$  in the present study is somewhat incompatible with the previous 50 study by Amezawa but it could be due to some kinetic reason. The present results indicate that the solubility of Sr in LaPO<sub>4</sub> would be sufficiently high (at least 20.1 %) at 600 °C, which is in the operating temperature range for the electrolyte. However, the solubility of Sr is considerably lower than



**Fig. 9** X-ray diffraction patterns of (a) 13.4% Sr-doped LaPO<sub>4</sub> and (b) 20.1% Sr-doped LaPO<sub>4</sub>. They were collected (a-1)(b-1) just after washing, (a-2)(b-2) after the first heat treatment at 600 °C for 80 h and (a-3) after the second heat treatment at 1200 °C for 5 h. Peaks marked with  $\nabla$ ,  $\bullet$ , and  $\bigcirc$  are attributed to LaPO<sub>4</sub> (PDF# 1-83-651), Sr<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (PDF#0-24-1011), and Sr<sub>3</sub>La(PO<sub>4</sub>)<sub>3</sub> (PDF# 0-29-1306), respectively.

13.4 % at 1200 °C, which is a typical sintering temperature for this material. Therefore, a new synthesis process of LaPO<sub>4</sub> electrolytes based on precipitation in homogeneous phosphoric acid solutions, which enables synthesizing dense s LaPO<sub>4</sub> electrolytes without sintering, should have a great

advantage. The stability of Sr-doped LaPO<sub>4</sub> for longer periods will be the subject of future studies.

### 4. Conclusions

- In this study, we investigated the precipitation condition of <sup>10</sup> LaPO<sub>4</sub> in phosphoric acid solutions and the morphology of the precipitates. We also studied the optimum condition for obtaining highly Sr-doped LaPO<sub>4</sub>. Then we examined the effectiveness of doping. Finally we evaluated the stability of Sr-doped LaPO<sub>4</sub> at high temperatures. The findings can be <sup>15</sup> summarized as follows:
- (1) Increasing  $pH_2O$  from 0.01 atm to 1 atm extends the precipitation region of LaPO<sub>4</sub> in phosphoric acid solutions toward higher temperatures by nearly 100 °C. It is possible to obtain aggregated LaPO<sub>4</sub> crystals up to 200  $\mu$ m
- <sup>20</sup> under such conditions (*e.g.* T = 250 °C and  $pH_2O = 1$  atm). This may facilitate the direct synthesis of dense LaPO<sub>4</sub> electrolytes in phosphoric acid solutions.
- (2) The Sr doping level in LaPO<sub>4</sub> shows a strong dependence on the precipitation ratio of La,  $X_{La}$ . The Sr doping level is
- higher in the low  $X_{La}$  region, reaching 20 % at maximum. This value is one order of magnitude higher than the previously reported solubilities of Sr in LaPO<sub>4</sub>.
- (3) Sr partially substitutes for La in monazite-type LaPO<sub>4</sub> when synthesized in phosphoric acid solutions, as well as
- 30 by solid state reaction as reported in literature. On synthesis, H<sub>2</sub>O is certainly incorporated in the bulk by Sr doping.
- (4) The solubility of Sr in LaPO<sub>4</sub> would be sufficiently high (at least 20.1 %) even at 600 °C, which is in the operating
- temperature range for the electrolyte. However, it becomes considerably lower than 13.4 % at 1200 °C.

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