

Investigation of Li Dopant as a Sintering Aid for ScSZ Electrolyte for IT-SOFC

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ABSTRACT

In this study, the effects of small amounts (≤ 3 mol%) of Li doping on the sintering characteristics and electrochemical performance of $(\text{ZrO}_2)_{0.89}(\text{ScO}_{1.5})_{0.1}(\text{CeO}_2)_{0.01}$ (ScSZ) were investigated. By adding 3 mol% lithium, the densification temperature of ScSZ was reduced from the conventional temperature of 1400°C to 1200°C. It was found that Li doping also led to changes in the Zr:Sc ratio at the grain boundaries. Correspondingly, the dispersion of lithium zirconia at the grain boundaries accelerated the growth of ScSZ grains and increased the grain boundary resistance at temperatures below 450°C. At elevated temperatures of 450~750°C, the electrical conductivity of the ScSZ after doping remained almost unchanged under air and reducing atmospheres. These results suggest that the addition of lithium is promising for use in low temperature co-firing of ScSZ-based components for intermediate temperature solid oxide fuel cells.

Key words: Solid oxide fuel cells, Electrolyte, Scandia stabilized zirconia, Sintering additions, Densification, Electrical conductivity

1. Introduction

$(\text{ZrO}_2)_{0.89}(\text{ScO}_{1.5})_{0.1}(\text{CeO}_2)_{0.01}$ (ScSZ) is a promising electrolyte for intermediate temperature (IT) solid oxide fuel cells (SOFCs) because of its high oxide-ion conductivity as well as its excellent chemical and physical stability under oxidizing and reducing atmospheres at intermediate temperatures.¹⁾ In the intermediate temperature regime, the electrolyte should be thinned in order to decrease the ohmic loss. To date, many processes have been suggested, including electrochemical vapor deposition (EVD), plasma spraying, screen printing, and pulsed laser deposition. However, the facile fabrication of the thin ScSZ membrane on a support remains a challenging issue. Among these processes, co-firing of the laminated electrolyte with the support as well as other components by using a wet-ceramic coating is particularly attractive due to its low manufacturing cost and mass productivity.²⁾ Establishing fabrication processes for the component materials, (the cathode, the electrolyte and the anode) at low sintering temperature is advantageous not only for lowering the cost but also for decreasing the reactivity among the component materials. However, achieving full density for ScSZ by conventional sintering methods using the wet-coating technique generally requires high temperatures exceeding 1400°C.³⁾ Nano-powders with a very large surface area can increase the driving force for

sintering, promoting and allowing densification to occur primarily via grain-boundary diffusion instead of lattice diffusion. On the other hand, dopants as sintering aids are also effective for lowering the sintering temperature of electrolytes. Several reports have discussed the relationship between dopants and densifications.⁴⁻⁸⁾ This relationship follows the equation $J = MC\nabla\mu$, where J is the flux of atoms along the grain boundary, M is the atomic mobility along the grain boundary, C is the vacancy concentration, and μ (the gradient in the chemical potential between the particle necks and a free surface) is the driving force for sintering. Dopants can increase one or more of the above parameters to lower the sintering temperature. This can be explained by several models. For example, the conversion of dopants into the liquid phase may alter M and increase $\nabla\mu$ due to capillary effects. Dopant substitution into the near grain boundary region also can alter M or C . Moreover, dopant segregation from the grain boundaries can alter M due to the formation of a second phase. These factors can greatly contribute to the lowering of the sintering temperature of an electrolyte.

It has been reported that various sintering aids including transition metal oxides⁶⁻¹⁰⁾ and other oxides^{11,12)} may increase the rate of densification for electrolytes. Among them, doping with 3 mol% lithium was reported to have the most obvious effect on the sintering of doped ceria.⁸⁾ The aim of this paper is to elucidate the sintering behavior of ScSZ doped with small amounts of lithium. The sintering and crystal characteristics as well as the thermal and electrical properties of the doped ScSZ were further investigated.

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2. Experimental

2.1. Preparations of Li-doped ScSZ and investigations of sintering behaviors

The $(\text{ZrO}_2)_{0.89}(\text{ScO}_{1.5})_{0.1}(\text{CeO}_2)_{0.01}$ (ScSZ) powder was commercially available ($10 \text{ m}^2/\text{g}$, Daiichi Kigenso Kagaku Kogyo, Japan). The ScSZ powder was mixed with Li_2CO_3 (Wako Pure Chemical Industries, Ltd., Japan) with the aid of water and ethanol (3:7 by volume). The ratio of Li to ScSZ ranged from 1 to 3 mol%. These mixtures were vigorously stirred for 30 min and further dried at 80°C . To investigate sintering characteristics, the as-prepared powders were pressed into discs of 20 mm diameter and 2~3 mm thickness by uniaxial dry pressing at 23 MPa. This was followed by sintering at selected temperatures between 600 and 1400°C with a heating/cooling rate of 200°C h^{-1} . The dimension and weight of the unfired and sintered discs were measured to determine the bulk density and the shrinkage. The theoretical density was calculated using the experimental lattice parameters and unit formula determined by X-ray diffractometric (XRD) analysis. The relative density was derived from the ratio of the bulk density to the theoretical density. The shrinkage of the discs was determined as $(d_1 - d_2)/d_1$, where d_1 and d_2 are the initial and final diameters, respectively. The crystal structure was confirmed by powdered X-ray diffraction (18 kW, Rigaku, ultraX 18TTR2-300, Japan). The microstructure of the sintered samples was recorded by scanning electron microscopy and energy dispersive X-ray analysis (EDX) (Hitachi, S-3500H, Japan).

2.2. Electrical performance measurements

Electrical conductivity was measured by the four-terminal method. The sintered species were cut into rectangular bars with dimensions of approximately $4 \times 4 \times 13 \text{ mm}^3$. The potential and current leads were contacted by applying platinum paste and fixing platinum. The conductivity was measured under hydrogen (saturated with H_2O vapor at 20°C) and air, respectively. A flow rate of 100 mL min^{-1} was used. The measurements were carried out at temperatures between 450 and 750°C . The conductivity at the relatively low

temperature of 400°C was measured by AC impedance using a Solartron 1260 frequency response analyzer with a 1296 interface. In this measurement, sample discs of 0.5~1 mm thickness were used.

3. Results and Discussion

3.1. Effect of Li addition on the crystal structure and sintering behavior of ScSZ

The XRD patterns of the $(\text{ZrO}_2)_{0.89}(\text{ScO}_{1.5})_{0.1}(\text{CeO}_2)_{0.01}$ (ScSZ) powders with different amounts of Li dopant sintered at 1200°C without holding time are shown in Fig. 1(a). As shown, the main crystal structure of ScSZ was stabilized to a cubic structure for all Li-doped samples. No second phases were observed, suggesting that part of the lithium could form a solid-solution with ScSZ and/or that the state of lithium could be amorphous. Fig. 1(b) shows the calculated lattice parameters and cell volume of ScSZ as a function of the amount of Li doping. The cell volume of ScSZ increased for 1 mol% and 2 mol% Li doping, and clearly decreased as the amount of lithium increased to 3 mol%. This indicates a possibility that the solid solution of cubic Sc_2O_3 -doped zirconia with lithium is limited to doping below 3 mol%.

As reported by Nicholas *et al.*,⁸⁾ the addition of 3 mol% lithium to $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ can significantly improve the sintering characteristics of the ceramic, achieving full densification at a remarkably low temperature of 800°C . This result was attributed to the presence of lithium in the liquid phase during sintering. Fig. 2 shows the thermal cycle of heating and cooling for ScSZ with 3 mol% Li_2CO_3 at temperatures of $400\sim 1200^\circ\text{C}$. The Li-doped ScSZ was reported to have several thermal stages of Li_2CO_3 at approximately 618°C , where portions of Li_2CO_3 decomposed to Li_2O and CO_2 . In the DTA curve, this peak was not observed due to the small amount of material in the samples. However, TG measurements showed a slow decrease in weight at approximately 610°C . Furthermore peaks were observed at 628 and 693°C due to Li_2CO_3 or Li_2O beginning to melt. Note that the reported melting point of Li_2CO_3 is 723°C , which is

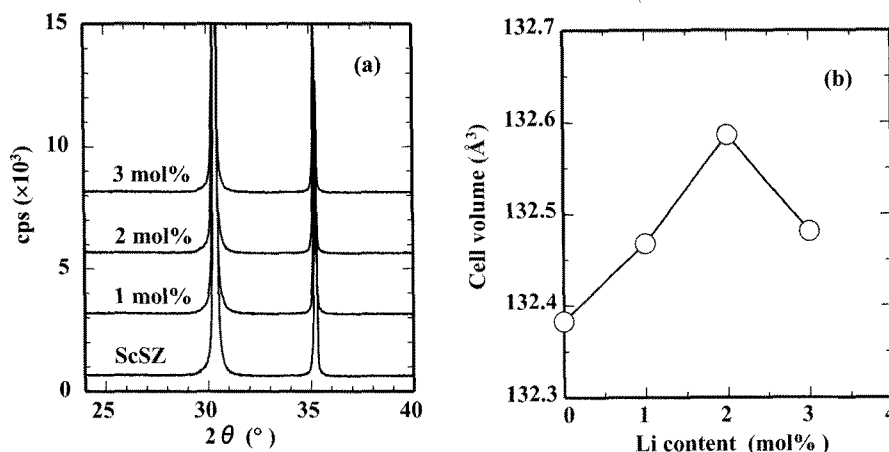


Fig. 1. XRD patterns (a) and cell volume (b) of ScSZ with different amounts of lithium addition.

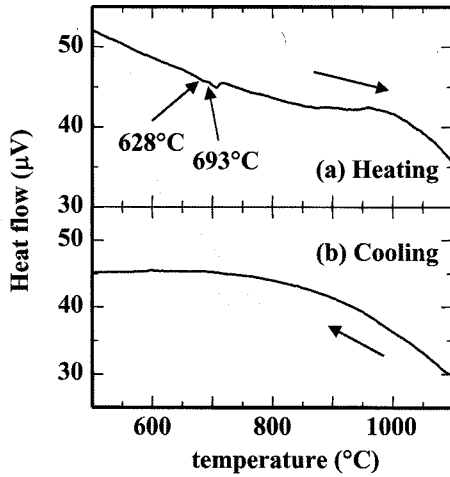


Fig. 2. DTA curves of ScSZ with 3 mol% Li_2CO_3 in air.

slightly higher than the currently observed value. This might be due to the dispersion state of Li_2CO_3 as well as its interaction with ScSZ.

The effects of 0.2~1 mol% Li doping on the sintering behavior of ScSZ are shown in Figs. 3(a) and (b). The addition of 0.2 mol% lithium did not have a noticeable effect on the densification of ScSZ, whereas 0.5 mol% and 1 mol% lithium considerably promoted the densification of ScSZ, as

shown in Fig. 3(a). As a result, the relative density of 1 mol% Li-doped samples reached over 90% at 1200°C without holding time, whereas the relative density of the non-doped ScSZ sample was approximately 80%, as shown in Fig. 3(a). The densification of Li-doped ScSZ at 1200°C can be further increased to over 95% by increasing the doping amount of lithium to 3 mol% and increasing the holding time to 3 h. Accelerated densification generally increased the shrinkage of the sintered body, as shown in Fig. 3(b), where 0.5 mol% and 1 mol% Li doping clearly resulted in a higher shrinkage of the ScSZ. It was confirmed that the maximum effects were observed when the dopant amount was around 3.0 mol%.

Fig. 4(a) shows the microstructure of a non-doped ScSZ sample sintered at 1200°C for without holding time. The micrograph reveals a porous structure with relatively low densification. After 3 mol% Li doping, dense polygonal grains with fewer pores and an approximate grain size of <math><1\ \mu\text{m}</math> were observed, as shown in Fig. 4(b). It is clear that Li doping greatly improved densification of ScSZ.

The effects of holding times at 1200°C on Li-doped ScSZ samples were also investigated. As confirmed by the SEM observations shown in Fig. 5(a), the grain sizes of ScSZ increased from 0.6~0.8 μm for non-doped ScSZ, to around 1~2 μm for 3 mol% Li-doped ScSZ after sintering at 1200°C

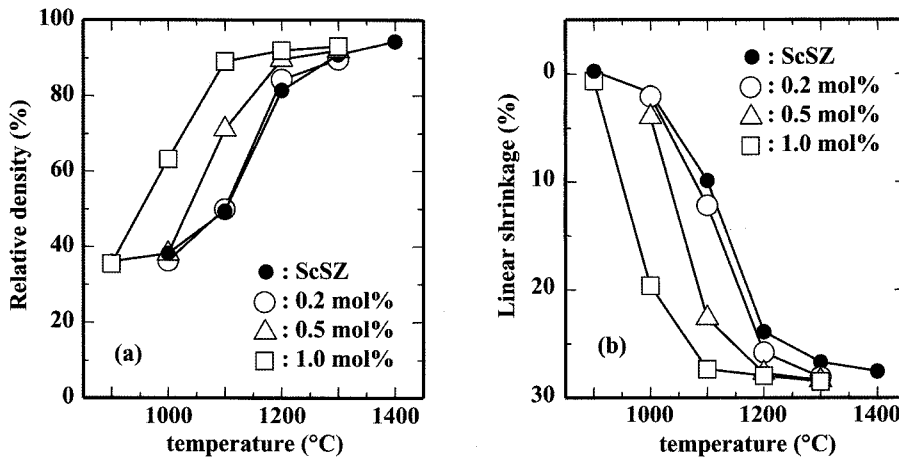
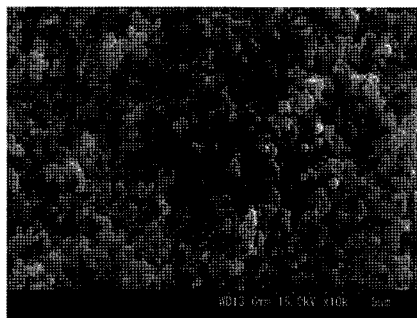


Fig. 3. Relative density (a) and shrinkage (b) of Li-doped ScSZ samples as a function of sintering temperature.



(a) ScSZ



(b) 3 mol% Li_2CO_3 doped ScSZ

Fig. 4. SEM micrographs of non-doped ScSZ (a) and 3 mol% Li-doped ScSZ (b) at 1200°C without holding time.

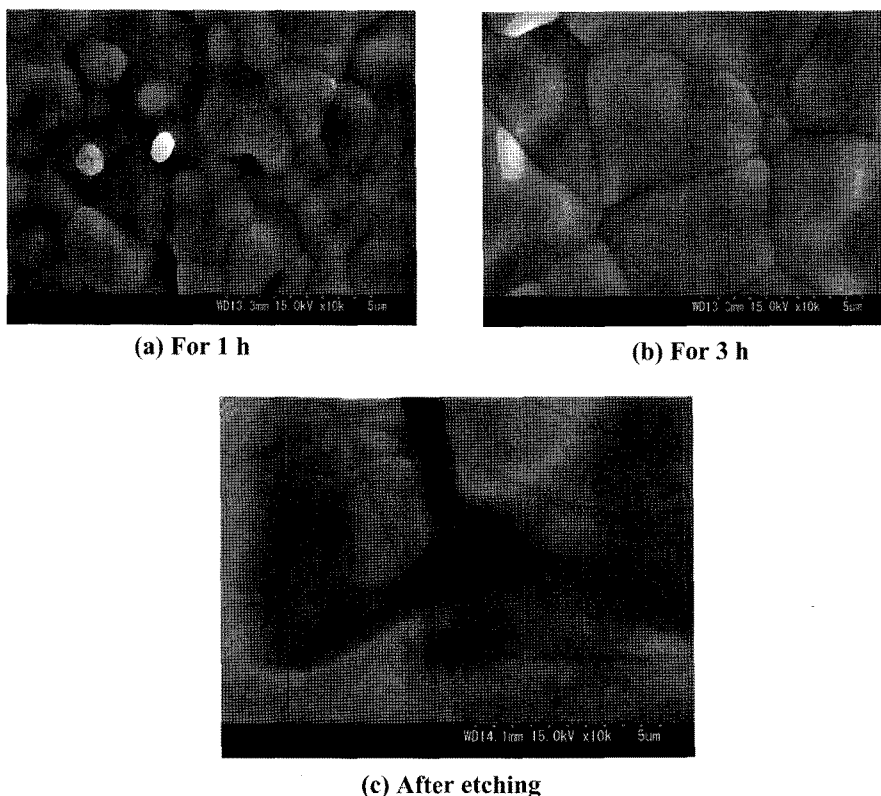


Fig. 5. SEM micrographs of the dense body of 3 mol% Li-doped ScSZ sintered at 1200°C for (a) 1 h, (b) 3 h, as well as (c) after etching of (b).

for 1 h. Increasing the holding time to 3 h enlarged the grain sizes to 3~5 μm, as shown in Fig. 5(b). This suggests that a liquid phase was formed during the sintering. The addition of lithium to ScSZ is effective for low temperature co-firing of SOFC components. Fig. 5(c) shows the SEM micrograph of the enlarged area at the grain boundary of the dense body of a 3 mol% Li-doped ScSZ sample sintered at 1200°C for 3 h and further etched with nitric acid. The removal of lithium left a clear groove with an average width of 500 nm, suggesting that the residual lithium could

agglomerate at the grain boundaries during the sintering. We postulated that the addition of 3 mol% lithium into ScSZ mainly accelerated the densification of ScSZ by increasing the driving force for sintering, promoting and allowing densification to occur primarily via grain boundary diffusion.

Fig. 6 shows the thermal expansion curves of ScSZ and 3 mol% Li-doped ScSZ in air. No obvious change was observed suggesting that the addition of lithium does not negatively affect the thermal behavior of ScSZ. The thermal expansion coefficients at 50~650°C for non-doped ScSZ and Li-doped ScSZ were $9.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $9.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, respectively. These values were consistent within experimental error.

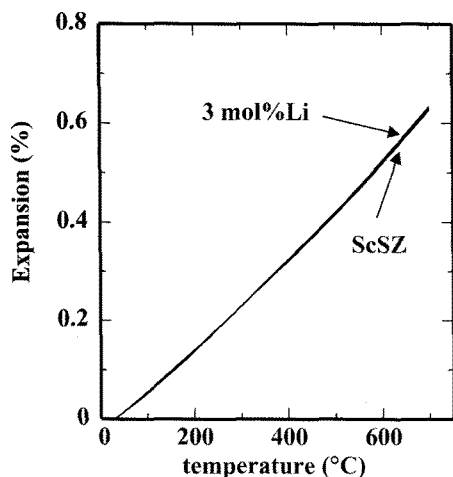


Fig. 6. Expansion curves of ScSZ and 3 mol% Li-doped ScSZ in air.

3.2. Electrical performance of ScSZ with Li doping

Fig. 7(a) shows the complex impedance plane plots of ScSZ and 3 mol% Li-doped ScSZ at 400°C in air. The depressed semicircle can be attributed to the combination of bulk and grain boundary resistances. The semicircle at relatively high frequencies represents the bulk resistance and the semicircle at relatively low frequencies presents the grain boundary resistance, whereas the linear slope at very low frequencies shows the resistance of the electrode. Fig. 7(b) summarizes the simulation data of Fig. 7(a) and shows the bulk (R_b) and grain boundary (R_g) resistance of ScSZ and 3 mol% Li-doped ScSZ as a function of temperature in air. The effect of lithium addition on the lattice oxide-ion conductivity was not very remarkable, while the influence on

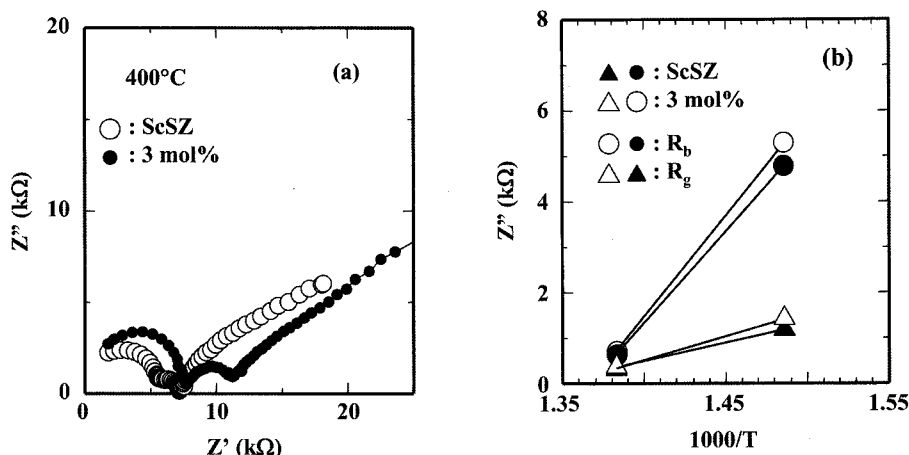


Fig. 7. (a) Complex impedance plane plots of the ScSZ and 3 mol% Li-doped ScSZ at 400°C in air; (b) The bulk (R_b) and grain boundary (R_g) resistance of ScSZ and 3 mol% Li-doped ScSZ in air.

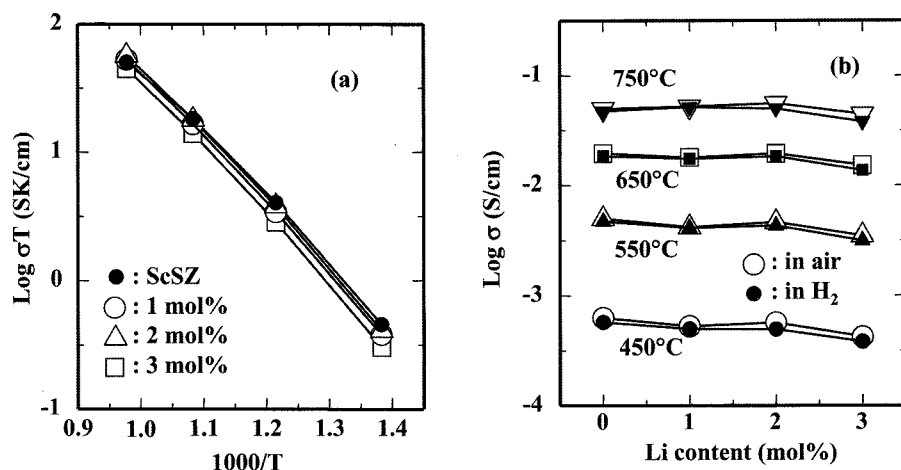


Fig. 8. (a) Temperature dependencies of the electrical conductivity of ScSZ with lithium addition in air; (b) Electrical conductivity of the doped ScSZ in air and in the 30% H_2 - N_2 atmosphere as a function of lithium dopant contents.

ScSZ reflected a major obstacle to oxide-ion conduction at the grain boundary. The grain boundary behavior cannot be described by a simple brick layer model, which predicts lower grain boundary resistance for larger average grain sizes. The electrical behavior of Li-doped ScSZ can be explained by the formation of a second phase of lithium-rich agglomeration at the grain boundary, as confirmed by Fig. 5.

Fig. 8(a) shows the electrical conductivity of ScSZ with different amounts of Li dopants in air as a function of temperature. It can be seen that the linear slopes of all the samples remain almost constant at all temperatures between 450 and 750°C and the values of the activation energy correspond highly with the results published earlier for ScSZ systems.¹⁾ Almost no significant change in the electrical conductivity was observed as the lithium concentration increased, suggesting that lithium mainly functions as a sintering aid for ScSZ.

Fig. 8(b) shows the electrical conductivity of ScSZ in air and in a 30% H_2 - N_2 atmosphere as a function of the amount of lithium dopants at temperatures of 450~750°C (open dot:

air; filled: reducing atmosphere). The slight increase of conductivity in the reducing atmosphere is thought to be negligible compared to the dopant effects. It was concluded that a small amount of lithium might not influence the electrolytic behavior of ScSZ when used in IT-SOFCs.

4. Conclusions

In this study, the sintering behavior of ScSZ electrolytes was studied using lithium as a sintering aid. Lithium agglomeration was dispersed at the grain boundary of ScSZ and considerably improved the densification of ScSZ. A highly dense body was obtained at 1200°C, compared to the conventional sintering temperature of 1400°C. The conductivity of the doped ScSZ electrolytes was lowered by resistive grain boundaries at temperatures below 450°C. At elevated temperatures, the electrical conductivity of ScSZ after doping remained almost unchanged under air and reducing atmospheres. These results suggest that lithium addition is promising for use in low temperature co-firing of

ScSZ-based components for IT-SOFCs.

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