Study of Nano-Composite Proton Conducting Membranes for an Intermediate-Temperature H_2S Solid Oxide Fuel Cell

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Abstract: Nano-composite proton conducting membranes of an intermediate-temperature H_2S solid oxide fuel cell were prepared using a sol-gel technique. The membranes have been characterized and observed using scanning electron microscope (SEM) and energy dispersive X-ray (EDX). Electrolyte performance prepared by a conventional route and a new technique of gel-solution preparation was compared. Relation of ionic conductivity performance of micro and nano-composite electrolytes of $Li_2SO_4 + Al_2O_3$ with temperature variation was explored. The microstructure, compactivity, mechanical strength, and conductivity of membranes were improved comparing with those of the same bulk composition prepared from mixtures of lithium sulfate as well as alumina powder. The remarkable enhancement in ionic conductivity was obtained for nano-composite $Li_2SO_4 + Al_2O_3$. The less gas crossover and better stability of an intermediate-temperature H_2S solid oxide fuel cell with nano-composite $Li_2SO_4 + Al_2O_3$ proton-conducting membranes were observed, and the maximum power density of up to 135 mW·cm^{-2} and maximum current density of about 480 mA·cm^{-2} were achieved at 750℃ and 101.13 kPa.

Key words: intermediate-temperature solid oxide fuel cell (ITSOFC); proton-conducting membrane; hydrogen sulfide
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H_2S is a severe pollutant that is a by-product of many industrial operations such as processing of natural gas, coking, and desulfurization of crude oil or coal. Treatment of H_2S is considered as a worldwide problem. Many processes have been developed to remove and recover H_2S, including adsorption and absorption, conversion to elemental sulfur, and oxidation to sulfur oxides. Fuel cell technology offers a means of electrochemical conversion of hydrogen sulfide for producing electricity and element sulfur[1-4]. The solid oxide proton-conducting membrane fuel cell is one of the most promising candidate fuel cells. In the present work, some new composite membranes using a Li_2SO_4-Al_2O_3 nano-composite prepared applying a customized sol-gel technique will be developed, and fuel cell performances between different membranes prepared using conventional procedure and sol-gel technique are compared.

1 Experimental

Two types of membranes with a designed composition were prepared using the following procedures. First is a conventional route (designated micro composite) for preparing ceramic materials. The appropriate amounts of Li_2SO_4 and Al_2O_3 (better weight ratio of Li_2SO_4 and Al_2O_3 60 : 40) were weighted and mixed well with a small amount of water[4]. The mixture was in the form of a paste, because the amount of water was insufficient to affect total dissolution. The paste was dried in air, and then ground to powder until the particle size was smaller than 25 μm. An aliquot of the powder was weighted (0.8 ~ 1 g), loaded into a mould with a diameter of 2.54 cm, pressed and sintered in air in an oven.

The anode and cathode materials used were a Mo-Ni-S-based composite anode, a NiO-based composite cathode. Details of the preparation of anode and cathode as well as a fuel cell test station are in ref [5]. Data were recorded with a Gamry electrochemical meas-

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urement system (PC4—750). EIS measurements were performed to determine cell resistance. Potentiodynamic measurements were conducted to determine the cell current-voltage performance in their compensation mode using the Gamry system at a scanning rate of 1 mV·s^{-1}[4-5].

2 Results and Discussion

2.1 Effect of particle size

Two sizes of alumina particles were used in the Li_2SO_4-Al_2O_3 compositions: micron (0.35 ~ 0.49 μm) α-Al_2O_3 from Alfa Aesar and nano-sized (about 20 nm) alumina prepared using our sol-gel procedure. Figs 1 and 2 show the SEM phones of micro and nano-sized membranes. A great number of voids, micro-defects, and cracks were seen in samples prepared using micro-composite Li_2SO_4-Al_2O_3 from Fig 1. In contrast, the number of micro-defects in the interfacial zone and bulk lithium sulfate matrix was significantly reduced, the density and compactibility were increased in samples prepared using nano-composite Li_2SO_4-Al_2O_3 from Fig 2.

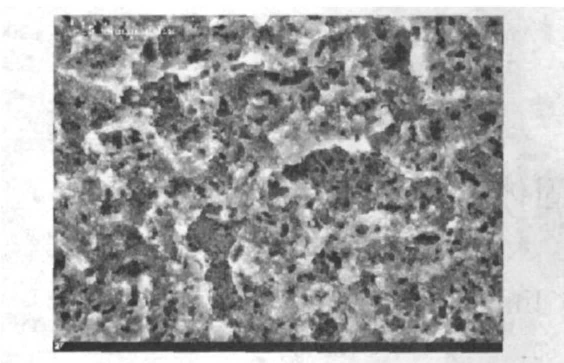

Fig 1 SEM image of micro-composite membrane of Li_2SO_4-Al_2O_3 at sintered temperature of 850℃

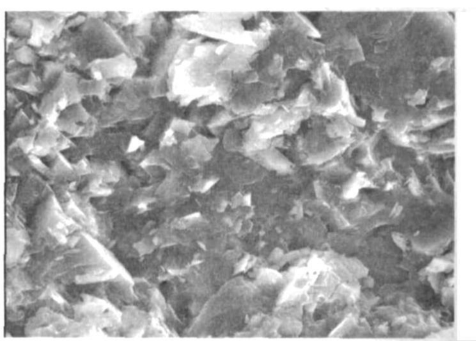

Fig 2 SEM image of nano-composite membrane of Li_2SO_4-Al_2O_3 at sintered temperature of 850℃

2.2 Conductivity

Electrical conductivity of micro and nano-composite samples at different temperatures is shown in Fig 3. It was found that the conductivity increased with temperature when the temperature is below 953 K. The conductivity kept almost the same while the temperature exceeded 953 K. The sample prepared from nano-composite Li_2SO_4-Al_2O_3 had electrical conductivity about 0.22 S·cm^{-1}, one order of magnitude higher than that reported for micro materials above 953 K due to the enhanced homogeneity and physical interfacial interaction between the nano-composite components, Li_2SO_4 and Al_2O_3.

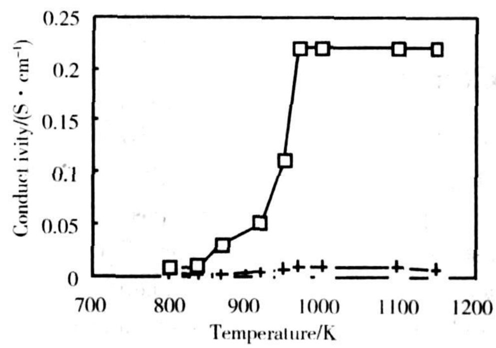

Fig 3 Temperature dependence of conductivity for membranes prepared by micro-composite and nano-composite materials
□: nano $Li_2SO_4+Al_2O_3$, +: micro $Li_2SO_4+Al_2O_3$

2.3 Fuel cell performance

Figure 4 exhibits the relationship of current density and power density for a cell with micro and nano membranes at 680 and 750℃, respectively. The maximum power and current densities of fuel cell for micro composite membrane were 40 mW·cm^{-2} and 200 mA·cm^{-2} at 680 ℃, and were 70 mW·cm^{-2} and 400 mA·cm^{-2} at 750 ℃, respectively. While the maximum power and current densities of fuel cell for nano composite membrane were 65 mW·cm^{-2} and 395 mA·cm^{-2} at 680℃, and were 135 mW·cm^{-2} and 480 mA·cm^{-2} at 750℃, respectively. The fuel cell of nano-composite membrane is superior to that of micro composite membrane since the former has higher electrical conductivity, more compactivity and less gas crossover. In addition, it also can be seen from Fig 4 that the increase of temperature can significantly improve the cell performance.

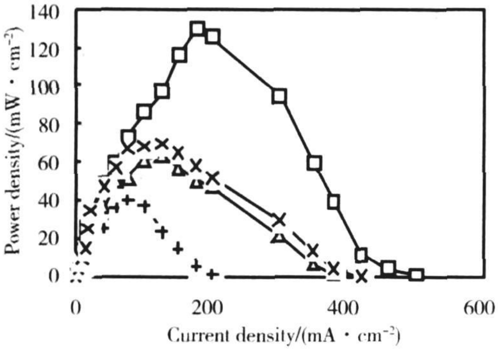

Fig. 4 Power density vs current density for nano and micro $Li_2SO_4+Al_2O_3$ membrane cells at various temperatures
750 ℃: □ nanomembrane, × micromembrane
680 ℃: △ nanomembrane, + micromembrane

3 Conclusions

A nano-composite Li_2SO_4-Al_2O_3 electrolyte has been prepared by applying a sol-gel technique. Membranes prepared using nano-composite Li_2SO_4-Al_2O_3 demonstrated high density and compactivity as well as conductivity about 0.22 S·cm^{-1} mainly due to the formation of an improved homogeneous microstructure and interfacial contact between Li_2SO_4-Al_2O_3 resulted from nano-particle size alumina. The appropriate ratio of Li_2SO_4 and Al_2O_3 is about 60:40 by weight and the heating treatment temperature of membranes is around 850℃. The fuel cell performance of nano-composite Li_2SO_4-Al_2O_3 electrolyte is superior to that observed in micro-composite Li_2SO_4-Al_2O_3 system.

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纳米复合质子传导膜中温硫化氢固体氧化物燃料电池的研究

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摘　要：应用溶胶-凝胶法制备了中温硫化氢固体氧化物燃料电池的纳米复合质子传导膜。用SEM和EDX对纳米复合膜进行了观察和表征，并与传统工艺制备的电解膜（微米级）的性能进行了比较。探讨了微米级和纳米级的复合$Li_2SO_4+Al_2O_3$膜的离子传导性随温度变化规律。与传统的工艺采用相同组分制备的微米级电解膜相比，纳米复合膜的微观结构、致密性、机械强度和离子传导性均得到改善，而最显著改善是膜的离子传导性能。纳米复合$Li_2SO_4+Al_2O_3$膜的中温硫化氢固体氧化物燃料电池的性能较稳定，察觉不到膜两侧的气体穿过膜扩散到另一侧。在750 ℃和101.13 kPa下，电池的最大输出功率密度为135 mW·cm^{-2}，最大电流密度为480 mA·cm^{-2}。

关键词：中温固体氧化物燃料电池；质子传导膜；硫化氢

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