

硫化氢燃料电池的无机质子传导膜与 MEA 制备和性能

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摘要: 制备了硫化氢固体氧化物燃料电池的无机质子传导膜和膜-电极-组装(MEA)。用扫描电镜(SEM)和电化学阻抗(EIS)技术表征了无机质子传导膜和 MEA 的形貌与性能。研究了不同膜厚和掺杂或没有掺杂 Li_2WO_4 组分的传导膜和 MEA 的性能。结果表明,与没有掺杂 Li_2WO_4 组分制备的 MEA 相比,掺杂了 Li_2WO_4 组分制备的 MEA 的电导提高了一个数量级,掺杂了 Li_2WO_4 制备的 MEA 硫化氢燃料电池在操作条件下具有更好的化学稳定性和电化学性能。以 Mo-Ni-S 为主要成分的复合阳极、0.8 mm 厚和组成为 67wt% Li_2SO_4 + 8wt% Li_2WO_4 + 25wt% Al_2O_3 复合材料制备的质子传导膜、NiO 为主要组分的复合阴极构成的 MEA 硫化氢燃料电池,在 650、700 和 750 °C 时,最大输出功率密度分别达到 50、85 和 130 $\text{mW}\cdot\text{cm}^{-2}$,最大电流密度分别为 200、350 和 480 $\text{mA}\cdot\text{cm}^{-2}$ 。

关键词: 膜-电极-组装(MEA); 质子传导膜; 固体氧化物燃料电池; 硫化氢

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Preparation and Performance of Inorganic Proton-conducting Membrane and MEA for H_2S Solid Oxide Fuel Cells

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Abstract: A membrane electrode assembly (MEA) for H_2S solid oxide fuel cells with inorganic proton-conducting membranes was prepared. Membrane or MEA has been characterized using scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS). Performances of membrane or MEA having various thicknesses and prepared with or without Li_2WO_4 component have been investigated. The results show that electrical conductance of MEA prepared with Li_2WO_4 -doped material is one order of magnitude higher than that of MEA prepared without Li_2WO_4 -doped material, and that MEA prepared with Li_2WO_4 -doped material has better chemical stability and electrochemical performance under the operating conditions of a fuel cell using H_2S as the fuel in comparison to MEA prepared without Li_2WO_4 -doped material. Maximum power densities of 50, 85 and 130 $\text{mW}\cdot\text{cm}^{-2}$, as well as maximum current densities of 200, 350 and 480 $\text{mA}\cdot\text{cm}^{-2}$ for the MEA configuration with a Mo-Ni-S-based composite anode, composite membrane (67wt% Li_2SO_4 + 8wt% Li_2WO_4 + 25wt% Al_2O_3) of 0.8 mm thick and a NiO-based composite cathode were achieved at 650, 700 and 750 °C, respectively.

Key words: membrane electrode assembly (MEA); proton-conducting membrane; solid oxide fuel cells (SOFCs); hydrogen sulfide

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0 Introduction

Hydrogen sulfide (H_2S), a corrosive and extremely toxic gas present in supply of natural gas, coal gasification, crude oil refining and geothermal energy at concentrations ranging from a few ppm ($\text{mg}\cdot\text{L}^{-1}$) to 50% or higher, is produced during desulfurization of hydrocarbon resources and is environmentally undesirable so that its decomposition is desired or required in many instances. There are various prior art methods for H_2S disposal. The oil refining industry, for example, uses a method known as the Claus process^[1-4]. The Claus process for oxidizing H_2S to sulfur dioxide and water (steam) is exothermic. The heat generated is generally not utilized, and the capital investment can not be economically justified. Other disadvantages of the Claus process are that its H_2S conversion efficiency is only about 92% and other pollutants, such as CS_2 and COS , are normally produced as well.

A solid oxide fuel cell using H_2S as fuel was first reported in 1987^[1]. Current development of H_2S solid oxide fuel cells (SOFCs) is mainly based on the electrolytes like oxide ion-conducting yttria-stabilized zirconia (YSZ) and proton-conducting membranes. When preferred proton-conducting membranes are used in an H_2S -air fuel cell, high-purity sulfur is the only product obtained in the anode chamber and water is the mere product formed in the cathode chamber. However, with oxide ion-conducting membranes, elemental sulfur, water and SO_2 are formed in the anode chamber requiring further removal of SO_2 . Peterson and Winnick, Wei et al.^[5,6] reported the use of Li_2SO_4 as proton-conducting electrolyte material in H_2S fuel cell. The H_2S fuel cell with Li_2SO_4 electrolyte had lower electrical conductivity, gas-permeability, and lower current and power density during the operation. The most challenge task for the development of H_2S fuel cell using a proton-conducting membrane is the development of a composite Li_2SO_4 -based proton-conducting membrane with high electrical conductivity, gas-impermeability and better performance. Gundushaurma et al.^[7] reported that the composite Li_2SO_4 material admixing Li_2WO_4 can improve its electrical conductivity and other

performance since a new solid phase, $\text{Li}_2\text{SO}_4 + \text{Li}_2\text{WO}_4$ is formed, which changes its molten point and electrical conductivity. Currently, no such H_2S fuel cell of composite membrane is commercially available. The focus of research on H_2S fuel cells in this work is therefore on the proton-conducting fuel cell, particularly in the preparation of composite Li_2SO_4 -based proton-conducting membranes admixing Li_2WO_4 as well as the development of a preparation method for membrane electrode assembly (MEA).

1 Experimental

1.1 Preparation of membranes

To prepare a composite membrane with a designed composition, $\text{Li}_2\text{SO}_4 + \text{Li}_2\text{WO}_4 + \text{Al}_2\text{O}_3$ or $\text{Li}_2\text{SO}_4 + \text{Al}_2\text{O}_3$ nano-composite components were prepared using a sol-gel technique developed in our laboratory for preparation of the target materials. Aluminum nitrate [$\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$], 98wt% (from Sigma-Aldrich Inc.), lithium sulfate anhydrous (Li_2SO_4), 99.7wt% (from Alfa Aesar Inc.), lithium wolframate anhydrous (Li_2WO_4), 99.8wt% (from Alfa Aesar Inc.) were used as starting materials for membranes. The technique comprised sequential steps of gel-solution preparation. Certain amount of Li_2SO_4 , Li_2WO_4 and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was weighed and dissolved in water. An aqueous solution formed was heated to 550 °C under stirring, water in the solution was evaporated while NO_x was escaped from the solution. The dry composite electrolyte materials so obtained were ground in a ball-grinding machine and then sintered at 700~850 °C to remove remaining NO_x in the electrolyte materials so as to obtain $\text{Li}_2\text{SO}_4 + \text{Li}_2\text{WO}_4 + \text{Al}_2\text{O}_3$ or $\text{Li}_2\text{SO}_4 + \text{Al}_2\text{O}_3$ nano-composite components, and the solid materials so formed were ground to required particle sizes ($<20\ \mu\text{m}$). Heat treatment parameters affected the mechanical strength of electrolyte. Lithium sulfate or lithium wolframate and alumina do not react chemically at sintering temperatures less than 1 200 °C^[8]. Alumina has a sequence of high temperature phase transformations, namely γ , κ , θ , and α as the temperature rises from 600 to 1 200 °C^[8]. The quality of the interphase contact improved when the $\text{Li}_2\text{SO}_4 + \text{Li}_2\text{WO}_4 + \text{Al}_2\text{O}_3$ nano-composite compo-

ment was used. The phase transformations and thermal stress during the heat treatment below the melting point of lithium sulfate and lithium wolframate mixture led to the appearance of micro pores as well as poor compactivity, and these defects were mainly in the contact zone in the bulk matrix of nano-composites that had agglomerated^[8,9]. The bulk matrix consisted of crystalline zones and agglomerates (at room temperature), while alumina was present in the nano-composite predominately as the metastable γ -phase at 700~850 °C. When the heat-treatment temperature was at least as high as the melting point (about 825 °C) of lithium sulfate and lithium wolframate mixture (90wt% Li_2SO_4 and 10wt% Li_2WO_4), there were remarkable changes to the composite structure and morphology. A melted phase caused physical interaction between the salts and alumina particles and agglomerates of tightly bonded alumina grains were observed^[9].

1.2 Preparation of MEA (membrane-electrode-assembly)

To prepare a MEA, anode catalyst, a Mo-Ni-S-based composite anode, prepared from 80wt% MoS_2 + NiS, (1:1 weight ratio), 5wt% Ag powder, 5wt% starch and 10wt% electrolyte, was first put onto a 2.54 cm cylindrical die, followed by membrane materials (Li_2SO_4 + Li_2WO_4 + Al_2O_3 or Li_2SO_4 + Al_2O_3 nano-composite powder) containing suitable moisture content not to influence total dissolution, finally cathode catalyst, a NiO-based composite cathode, which was prepared from 80wt% NiO, 5wt% Ag powder, 5wt% starch and 10wt% electrolyte, was put onto the surface of membrane materials. The composite MEA sample disks were compressed for about 0.5 h under 250 MPa pressure. The MEA so obtained was then put in an oven and heated in nitrogen atmosphere, first at 105 °C for 90 min and then at 800~850 °C for 360 min. The MEA was cooled slowly to room temperature under nitrogen. The weight of MEA was approximately 10wt% less than the initial weight of the product due to the loss of water. The thickness of MEA is between 0.8 and 1.5 mm.

1.3 Installation of MEA into the fuel cell test station

A fuel cell test station was constructed, as shown

in Fig.1. To install the MEA assembly (2.54 cm diameter) into a test fuel cell, first the cathode side of the assembly was attached to a supporting annular alumina disk 3.2 cm in diameter and 0.3 cm in thickness using ceramic sealant (α -terpineol, from Aremco Product Inc.). An opening 1.1 cm in diameter in the center of the supporting ceramic disk allowed air to access the cathode. The combination so made was then sealed with ceramic sealant between two alumina tubular chambers (outer dimension 2.54 cm, length 40 cm), as described in References^[4,10,11]. An additional 3 mm wide sealant layer was applied around the sealing area to ensure a good seal. Platinum mesh was used as current collectors. The mesh surface was refreshed in the flame of a gas lamp prior to installation for each experiment^[4,6]. The cell was then heated in a tube furnace (Thermolyne F7930), with nitrogen passing through the anode chamber and air through the cathode chamber. To cure the sealant, the furnace temperature was increased at $0.8\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to 230 °C, and held at that temperature for 1 h. The temperature then was increased to a selected testing temperature, typically 600 °C, and held that temperature for the duration of each set of tests.

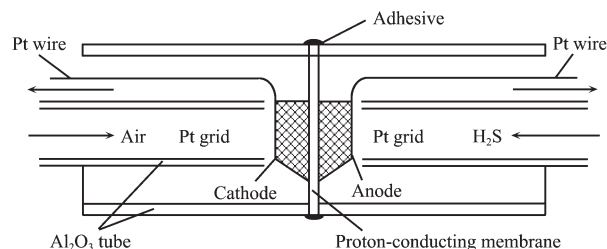


Fig.1 Fuel cell diagram

1.4 Characterization of membranes or MEA

Morphologies of membranes or MEA were studied with SEM technique using a Hitachi S-2700 Scanning Electron Microscope. Electrical conductivity of membrane or MEA was investigated with EIS technique. MEA was installed in the fuel cell test station, with Pt contacting leads attached to the anode and cathode of MEA. The resistance of each membrane or MEA was measured at selected temperature (500~750 °C). The temperature was adjusted (either increased or decreased) at $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to minimize thermal shock.

After a selected temperature had been maintained for 30 min, resistance data were acquired using conventional EIS methodology, and then electrical conductivity of membrane or MEA, at temperature of 500~750 °C and overall pressure of 101.3 kPa, can be calculated from the electrical resistance, the thickness and area of membrane (electrical conductivity=thickness of membrane/resistance of membrane area of membrane) under the operating conditions. Reaction products with [about 5% H₂O (partial pressure of water vapor is 5 kPa) and 95% air], were produced in the cathode chamber, while reaction products with about 3% S₂ and 97% H₂S were produced in the anode chamber.

1.5 Measurement of H₂S solid oxide fuel cell performance

Cell performance was determined using pure H₂S with flow rate of 50 mL·min⁻¹ as the anode feed, air with flow rate of 50 mL·min⁻¹ as the cathode feed. The cell open circuit voltage (OCV) was monitored as a function of time on stream. Data were recorded with a Gamry Electrochemical Measurement System (PC4-750). Initial electrical performance data were evaluated to determine cell integrity. Typically, a cell with no leaks showed a steady OCV value after about 30 min. A fluctuated, or a persistently low value (0.5~0.6 V) OCV, indicates possible leaks in the cell, and no further tests were conducted using that MEA. Potentiodynamic measurements were carried out to determine the cell current-voltage and current-power performance in their compensation mode using the Gamry system at a scanning rate of 1 mV·s⁻¹[4,9-11].

2 Results and discussion

2.1 Moisture of membranes

Three levels of moisture content of the mixtures were used during molding of powder mixtures: wet mixture (excess water wrings while pressing); semi-dry mixture, with water content no greater than that the powder can absorb from humidified air; and dry mixture (dried to constant weight at 105 °C). The highest degree of compression and the microscopically most homogeneous structure of samples were obtained for two cases:

pressing the wet mixture and the semi-dry mixture prepared using Li₂SO₄ + Li₂WO₄ + Al₂O₃ or Li₂SO₄ + Al₂O₃ nano-composite powder. However, the presence of high water content in molding mixtures caused formation of micro aggregates. Elevation of moisture content led to an increase in porosity and micro-cracks between the aggregates after the samples had been heat-treated. It is found that the optimal content of moisture in the nano-composite powder is in the range of 8%~10% by weight.

2.2 Composition of the formulation

The lithium sulfate and lithium wolframate content of the composite membrane was a critical factor affecting the composite properties. The compositions of lithium sulfate and lithium wolframate were determined for improvement of ion conduction. From the phase diagram of lithium sulfate and lithium wolframate considering cell operating temperature range and ion conductivity, suitable contents of lithium sulfate and lithium wolframate are around 90wt% Li₂SO₄ and 10wt% Li₂WO₄. Membranes made of only lithium sulfate and lithium wolframate were fragile, and very difficult to obtain an integral wafer by pressing. Thus alumina was required to confer strength to the composite. However, there was a decrease in conductivity when the lithium sulfate and lithium wolframate content in the composite Li₂SO₄ + Li₂WO₄ + Al₂O₃ membrane was less than 40%. The structure of MEA was deteriorated and its shape became deformed when the lithium sulfate and lithium wolframate content was as high as 80wt%, for all preparative conditions. Consequently, for the present study, the lithium sulfate and lithium wolframate content was between 60wt% and 80wt%, while alumina content was between 20wt% and 40wt% in all formulations. The experimental data, including membrane tightness and homogeneity as well as compactivity, MEA integral and fuel performance, revealed that the optimum composition of composite membrane was about 67wt% Li₂SO₄, 8wt% Li₂WO₄ and 25wt% Al₂O₃, respectively, in our study.

2.3 Morphologies of membranes

Following preliminary inspection of membranes with optical microscopy, the membrane morphology was

investigated with SEM technique. A SEM image of the membrane prepared from binary mixture of 75wt% Li_2SO_4 and 25wt% Al_2O_3 is shown in Fig.2A. Cavities pervaded throughout the membrane, and some cracks were visible on the surface. Fig.2B exhibits a SEM photograph of the membrane prepared from the 67wt% Li_2SO_4 , 8wt% Li_2WO_4 and 25wt% Al_2O_3 mixture. Cavities and boundary gaps are clearly reduced compared to the membrane prepared without Li_2WO_4 -doped component.

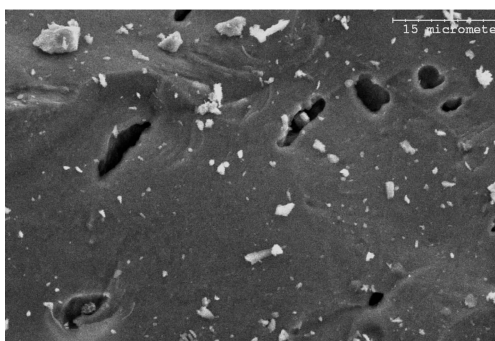


Fig.2A SEM image without Li_2WO_4 -doped membrane

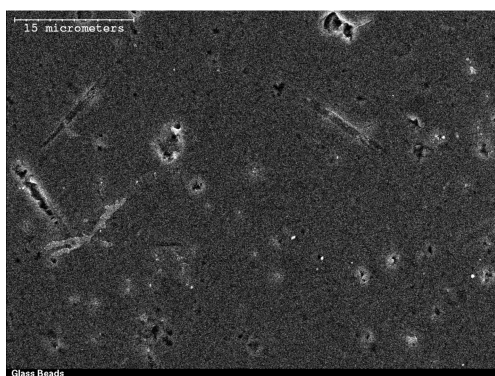
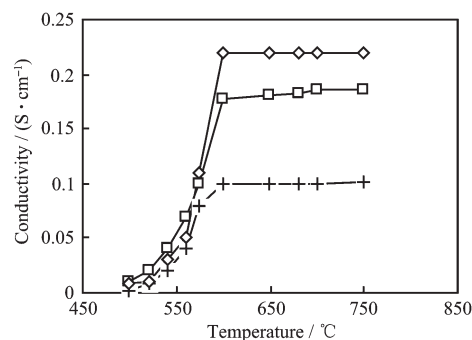


Fig.2B SEM image with Li_2WO_4 -doped membrane

2.4 Electrical conductivity of membranes

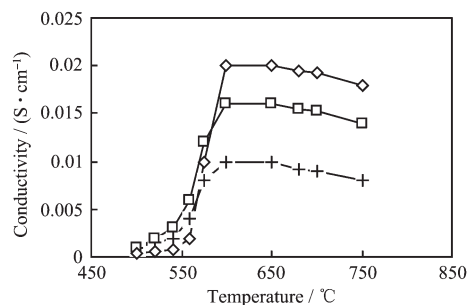
Electrochemical impedance spectroscopy (EIS) was used to study the change in the membrane electrical conductivity with temperature. Figs.3 and 4 show the conductivity as a function of temperature for different thicknesses of membrane (or MEA) prepared with or without Li_2WO_4 -doped material. An abrupt change in the MEA conductivity occurs at about 575 °C. The abrupt temperature is almost the same for each membrane, no matter the material is with or without Li_2WO_4 -doping. Conductivity increases little with temperature above 575 °C. Below 575 °C, it decreases dramatically. This indicates that 575 °C is the lowest

operating temperature appropriate for the present proton-conducting membranes. This phenomenon is attributed to the Li_2SO_4 phase transformation known to occur at 577 °C^[5]. It can be speculated that the operating temperature increase leads to enhanced electrical conductivity of the composites^[6,9,11]. All composite membranes prepared with Li_2WO_4 -doped material has one order of magnitude higher electrical conductivity than that prepared without Li_2WO_4 -doped material for the same membrane thickness. The considerably higher electrical conductivity for composite membranes from Li_2WO_4 -doped material can be attributed to the enhanced homogeneity and physical interfacial interaction between the nano-composite components, Li_2SO_4 , Li_2WO_4 and Al_2O_3 . It is seen from Fig.3 that a little increase of electrical conductivity for Li_2WO_4 -doped composite membranes is observed over 700 °C, but the electrical conductivity for membranes without Li_2WO_4 -doping is reduced at above 680 °C. The working temperature range of MEA cell prepared with Li_2WO_4 -



Membrane thickness ◇: 0.8 mm; □: 1.0 mm; +: 1.5 mm

Fig.3 Change of conductivity/thickness with temperature for 67wt% Li_2SO_4 , 8wt% Li_2WO_4 and 25wt% Al_2O_3 membranes



Membrane thickness ◇: 0.8 mm; □: 1.0 mm; +: 1.5 mm

Fig.4 Change of conductivity/thickness with temperature for 75wt% Li_2SO_4 and 25wt% Al_2O_3 membranes

doped material would be larger than that prepared without Li_2WO_4 -doped material, which is in agreement with the phase diagram of lithium sulfate and lithium wolframate^[8]. It is also seen from Fig.3 that electrical conductivity of MEA increases with the decrease of MEA thickness. Although thin membranes or MEA are preferred, there exist crossover and gas-permeability in MEA. The suitable MEA thickness is between 0.8 and 1.0 mm in our study.

2.5 Fuel cell performance

Fig.5 and 6 demonstrate the performance of fuel cell for a cell configuration of H_2S , ($\text{MoS}_2/\text{NiS} + \text{Ag} + \text{electrolyte} + \text{starch}$) /membrane prepared with and without Li_2WO_4 -doped material, thickness of 0.8 mm/($\text{NiO} + \text{Ag} + \text{electrolyte} + \text{starch}$), air at 650~750 °C, respectively. It is observed from the data in Figs.5~6 that maximum current and power densities are 200, 350 and 480 $\text{mA} \cdot \text{cm}^{-2}$, and 50, 85 and 130 $\text{mW} \cdot \text{cm}^{-2}$ for the fuel cell with Li_2WO_4 -doped material, 170, 230 and 290 $\text{mA} \cdot \text{cm}^{-2}$, and 35, 55 and 75 $\text{mW} \cdot \text{cm}^{-2}$ for the fuel cell without Li_2WO_4 -doped material at 650, 700 and 750 °C, respectively, which are close to the maximum power and current densities achieved by YSZ (oxide ion-conducting membrane) H_2S fuel cell at 800~850 °C^[10,12] although the operating temperature of the former is lower than that of the latter. The MEA prepared with the Li_2WO_4 -doped material has superior performance. In addition, it also can be seen from Figs.5~6 that the increase of temperature can significantly improve the cell performance. This is due to the characteristics of mass-transport limitation in electrochemical reaction^[13]. The effect is greatly reduced when the temperature is increased to 700 °C. This is probably due to the preoccupied active sites in anode by sulfur molecules at low operation temperature, which makes fuel gas difficult to reach the triple-phase boundary, the reaction area. At 700 °C, the rate of H_2S desorption and transport of sulfur from the vicinity of the active sites is increased, thus enhancing the electrochemical reaction rate, the combined effect of these changes improves cell performance. As far as the stability of cell with Li_2WO_4 -doped material and without Li_2WO_4 -doped material is concerned, the cell is run continuously for 12 h. The

relation of current density and time at the operating temperature of 700 and 750 °C is presented in Fig.7. Cell performance for MEA prepared with Li_2WO_4 -doped material is stable during the period of operation, while cell performance for MEA prepared without Li_2WO_4 -doped material degrades due to the crossover of H_2S and it becomes fast particularly at 750 °C. Some sulfide

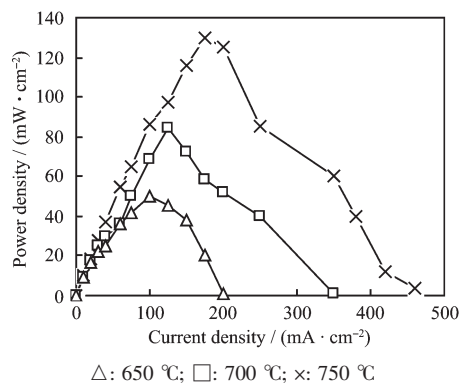


Fig.5 Performance of MEA (0.8 mm thick) prepared with Li_2WO_4 -doped material at different temperatures

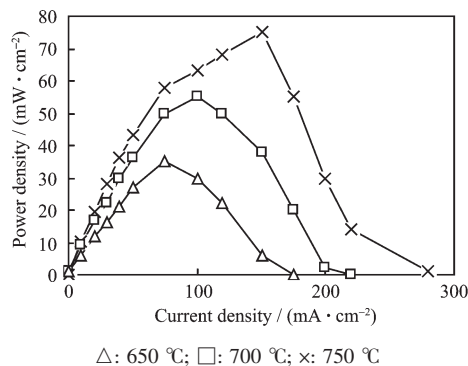
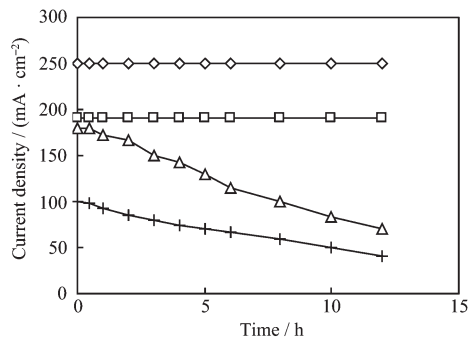


Fig.6 Performance of MEA (0.8 mm thick) prepared without Li_2WO_4 -doped material at different temperatures



+: MEA prepared without Li_2WO_4 -doped material at 700 °C;
△: MEA prepared without Li_2WO_4 -doped material at 750 °C;
□: MEA prepared with Li_2WO_4 -doped material at 700 °C;
◇: MEA prepared with Li_2WO_4 -doped material at 750 °C

Fig.7 Stability test of cell

deposited on the surface of cathode is visible when the cell is dismantled after experiments. The addition of Li_2WO_4 material improves the properties of composite membranes and increases the cell operating temperature. The results achieved so far have suggested that the composite MEA prepared with Li_2WO_4 -doped material is successful and has the wide operation temperature range for developing H_2S fuel cells with inorganic proton-conducting membranes.

3 Conclusions

The suitable preparation conditions have been determined for membrane electrode assembly (MEA). Addition of Li_2WO_4 to $\text{Li}_2\text{SO}_4\text{-Al}_2\text{O}_3$ mixture before preparing the membrane provides some benefits. Membranes prepared with Li_2WO_4 -doped material have good integrity, compactivity, tightness and homogeneity. MEA comprising 67wt% Li_2SO_4 , 8wt% Li_2WO_4 and 25wt% Al_2O_3 membranes has higher electrical conductivity and electrochemical performance than that prepared without Li_2WO_4 -doped material. Experimental results suggest that the MEA with a Mo-Ni-S composite anode, Li_2SO_4 -based nano-composite membranes doped with Li_2WO_4 , and a NiO-based composite cathode is identified as the suitable candidate for use as a H_2S SOFC.

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