Solid State Ionics 181 (2010) 1303–1307

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Compatibility analysis of Ag and electrolyte materials for LT-SOFCs and LT-SOECs

Kazuya Sasaki [a,*], Minoru Muranaka [a], Takayuki Terai [a,b]

[a] Department of Nuclear Engineering and Management, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0032, Japan
[b] Institute of Engineering Innovation, School of Engineering, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

ARTICLE INFO

Article history:
Received 3 March 2010
Received in revised form 9 July 2010
Accepted 11 July 2010

Keywords:
Solid oxide fuel cells (SOFCs)
Solid oxide electrolysis cells (SOECs)
Ag, scandia-stabilized zirconia (ScSZ)
Compatibility

ABSTRACT

The possibility of the use of Ag as the electrode material of low-temperature operating solid oxide fuel cells and low-temperature operating solid oxide electrolysis cells was researched by compatibility of Ag with electrolyte materials point of view. When a high anodic-potential (≥300 mV) is applied on a Ag electrode on a scandia-stabilized zirconia (ScSZ) electrolyte at 500 °C in dry O_2, Ag particles were deposited along the ScSZ grain boundaries. The phenomenon was specific to the Ag electrode on the ScSZ electrolyte. Because the phenomenon causes the electrical short between the cathode and the anode during the long time use, Ag is not appropriate as the anode side electrode (catalytic electrode or the current collector electrode of the anode side) of the actual low-temperature operating solid oxide electrolysis cells.

1. Introduction

In the energy market in the world, the crude oil price has soared by the stringent demand supply due to the increase in the oil demand and the decrease in the surplus of supply capacity of the oil-producing country and rises of the geopolitical risk of mideast situation. This tendency will extend for a long term in the future. The international energy situation has become aggravated like this. It is one of the effective means to reduce the dependence on the fossil fuel in primary energy, and to raise the nuclear power generation dependancy for the energy security improvement. However, the follow of the amount of power generation suited to demand is difficult in nuclear power generation. Therefore, when the energy consumption changes between seasons and day and night, the energy storing system that contributes to the stabilization of the energy supply and demand is requested.

The solid oxide electrolysis cells (SOECs) is a hydrogen generation device by the high-temperature electrolysis of steam. The SOECs enables to reduce the electrolysis voltage of the steam, because part of the energy can be directly supplied as thermal energy. That is, the SOECs is one of the efficient devices to produce a pure hydrogen. Solid oxide fuel cells (SOFCs) is a reverse-driving of the SOECs. Therefore, the energy system that hydrogen is produced by the SOECs steam electrolysis using steam from a nuclear power plant at the electric power surplus and electricity is generated by the SOFCs at the electricity shortage is a promising candidate for the energy storage.

Because the heat rejection temperature is about 700 °C even in the case of the highest-temperature-operating nuclear reactor (high-temperature gas-cooled nuclear reactor), the operating temperature of the SOECs and the SOFCs in this system needs to be low. Ag-adding-cathode for the SOFCs is widely researched in order to reduce the cathode reaction resistance that is one of the maximum problems for lowering the operating temperature of the SOFCs [1–13]. However, the purpose of most researches is an improvement of the SOFCs cathode characteristic by the Ag addition, and there is little report concerning compatibility of Ag with the electrolyte material.

In the present study, compatibility of Ag with the candidate electrolyte material for LT-SOFCs and LT-SOECs (scandia-stabilized zirconia, yttria-stabilized zirconia, gadolinia-doped ceria, and lanthanum strontium gallate magnesite) is clarified.

2. Experimental

The powders of $Sc_{0.1}Ce_{0.01}Zr_{0.89}O_{1.95}$ ($ScSZ_{CeO2}$), $Sc_{0.11}Zr_{0.89}O_{1.945}$ ($ScSZ_{CeO2\text{-}free}$), 8 mol%Y_2O_3–92 mol%ZrO_2 (YSZ), $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) (Daiichi kigenso kagaku kogyo) and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM) (Seimi chemical) were used as starting materials for the preparation of the electrolyte pellets. The powders of $ScSZ_{CeO2}$, $ScSZ_{CeO2\text{-}free}$, YSZ, GDC and LSGM were pressed into pellets at 3.9 kN/cm^2 and sintered in air at 1450 °C for 3 h to prepare dence electrolyte pellets. The pellet surface was ground and buff-polished using waterproof emery papers (no. 320, 500, 1000, 1500, and 2000) and alumina powder particles (0.05 μm diameter) to a mirror surface, then washed by an ultrasonic cleaner using ethanol. The prepared pellets were 15–18 mm in diameter, 1.3–1.8 mm thick, and over 99% in relative density.

---

* Corresponding author.
E-mail address: sasaki@n.t.u-tokyo.ac.jp (K. Sasaki).

0167-2738/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2010.07.003

A pure Ag powder was prepared using L-ascorbic acid and silver-nitric acid, and the Ag powder particles were dispersed in an organic vehicle to form a Ag paste.

Porous Pt counter electrodes were prepared on one-side-surfaces of the pellets of ScSZ$_{\mathrm{CeO2}}$, ScSZ$_{\mathrm{CeO2\text{-}free}}$, YSZ, GDC and LSGM by firing a Pt paste (TR7907, Tanaka kikinzoku kogyo) at 1100 °C for 1 h. Porous Pt reference electrodes were also prepared on the side of the pellets by the same procedure. After preparation of the counter electrodes and the reference electrodes, dense and continuous Ag thin film working electrodes were prepared on the other surfaces of the pellets symmetrical to the counter electrodes by firing the Ag paste at 900 °C for 1 h. The thicknesses of the Ag working electrodes and the Pt counter electrodes were 1 µm and 5 µm, respectively. The diameter of the electrodes were 8–10 mm. A Ag mesh and a Pt mesh were used as the current collector electrodes for the Ag working electrode and the Pt counter electrode, respectively. Pt wires were used as the lead wires.

Potentials of from −500 mV to 500 mV were applied to the Ag working electrodes against the reference electrode in dry O_2 at 500 °C for 100 h. This potential was interrupted every 3 h and the electrolyte resistivity was measured by the ac impedance method. The ac impedance measurement was conducted by the three-terminal method using an electrochemical analyzer (Ivium Stat type 20 V/2.5A, Ivium). The potential application and the electrochemical measurement were conducted in a single chamber.

First, the color of the electrolyte pellets was visually confirmed after the heat treatment at 500 °C with the anodic potential applied to the Ag working electrode. The surface of the electrodes and the fractured cross section of the electrolyte pellets were then analyzed using a field emission scanning electron microscope (FE-SEM) (JSM7000F, JEOL Ltd.) and an energy dispersive spectroscope (EDX) (JED2300, JEOL Ltd.). Since particles were deposited along the ScSZ$_{\mathrm{CeO2}}$ grain boundaries in the Pt counter electrode side, the chemical state of the particles was analyzed by X-ray absorption fine structure (XAFS) (EXAC-820, Technos). After removing the Ag working electrode using the waterproof emery papers, the surface of the electrolyte was analyzed by X-ray diffraction (XRD) (MXP-3, MAC Science) in order to clarify the formation of a secondary phase and peak shift results from the change in the lattice constant.

3. Results and discussion

Fig. 1 shows the photo images of the ScSZ$_{\mathrm{CeO2}}$ pellets with the Ag working electrodes after the heat treatment at 500 °C for 100 h in dry O_2 with the potentials of −500 mV (cathodic 500 mV) to 500 mV (anodic 500 mV). When the applied-anodic potential was 300 mV or higher, colors in contoured part of the Pt electrodes were changed from white to orange. The color was not changed when the applied anodic-potential was low of 100 mV. Moreover, the color was also not changed when the applied potential to the Ag working electrode was cathodic one and zero.

Fig. 2 shows cross section photo images of the ScSZ$_{\mathrm{CeO2}}$ pellets of 300 mV and 500 mV. In Fig. 2, their surface photo images are also shown to clarify the positional relationship between the color-changed area and the electrodes. The color-changed area localized to the near area of the Pt counter electrode, and extended from the interface of the Pt counter electrode and the ScSZ$_{\mathrm{CeO2}}$ pellet toward the Ag working electrode with the applied electric potential value.

Fig. 3 shows SEM images of the fractured cross sections of the ScSZ$_{\mathrm{CeO2}}$ pellet after the heat treatment at 500 °C for 100 h with the anodic potential of 500 mV applied to the Ag working electrode. Fig. 3 (a) and (b) are corresponding to the white area near the Ag working electrode and the orange area near the Pt counter electrode, respectively. Some particles were existing along the grain boundaries of the ScSZ$_{\mathrm{CeO2}}$ particles in the orange area, whereas no particles were found in the white area. The element of the particles exisiting along the ScSZ$_{\mathrm{CeO2}}$ grain boundaries was identified to Ag by EDX analysis. Fig. 4 shows a result of the XAFS analysis of the orange area. In Fig. 4, a result of the XAFS analysis of a Ag foil is also shown for the comparison. From the comparison of these data, the particles existing along the ScSZ$_{\mathrm{CeO2}}$ grain boundaries are Ag metal particles.

Fig. 5 is SEM images and an EDX mapping image of the suraface of the Ag working electrode after the heat teratment at 500 °C for 100 h with the anodic potential of 500 mV. Some holes opened in the Ag electrode, which had been dense and continued thin film before the heat treatment with applying the electric potential, and fine particles remained in the holes (Fig. 5 (a)). Fig. 5 (b) is a magnified SEM image in the hole and Fig. 5 (c) is an EDX mapping image of the area shown in Fig. 5 (b). The fine particles remained in the hole was Ag. Existence of Ag was also confirmed on the surface of the ScSZ$_{\mathrm{CeO2}}$ pellet other than as the Ag particles. The results suggest that Ag also exists in the ScSZ$_{\mathrm{CeO2}}$ pellets as Ag ion. The Ag working electrode on the ScSZ$_{\mathrm{CeO2}}$ pellet after the heat treatment at 500 °C for 100 h with the anodic potential of 500 mV was removed using the emery papers, then the surface of the ScSZ$_{\mathrm{CeO2}}$ pellet was analyzed by XRD. There were neither any new peaks nor peak shifts corresponding to the formation of a secondary phase formed by a reaction of Ag and ScSZ$_{\mathrm{CeO2}}$. These results imply that the Ag-ion concentration in the white area of the ScSZ$_{\mathrm{CeO2}}$ pellet was not high enough for the detection by XRD analysis. However, the color change and the Ag particle deposition along the ScSZ$_{\mathrm{CeO2}}$ grain boundaries in the near side area to the Pt counter electrode were also happened, even when atmospheres of the Ag

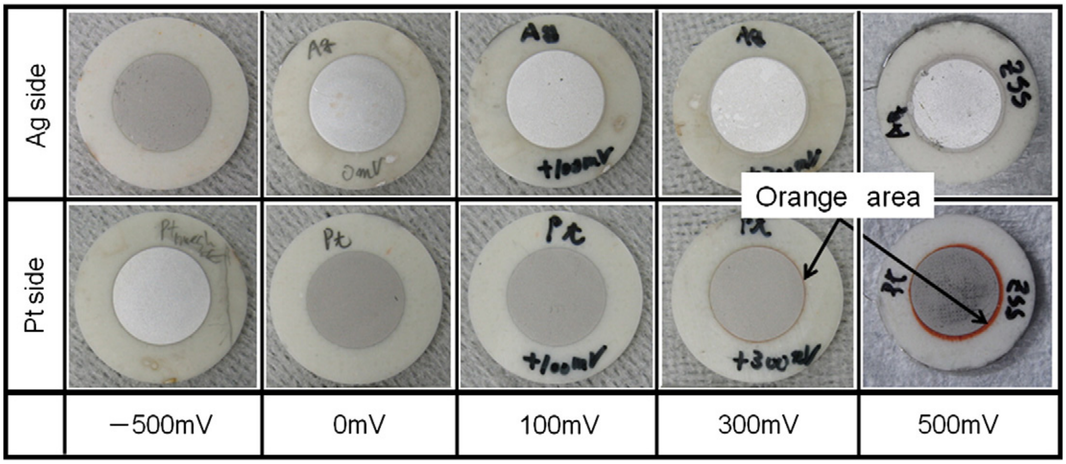

Fig. 1. Photo images of the ScSZ$_{\mathrm{CeO2}}$ pellets after the heat treatment at 500 °C for 100 h in dry O_2 with the potentials of −500 mV (cathodic) to 500 mV (anodic) applied to the Ag working electrode. (ScSZ$_{\mathrm{CeO2}}$: $Sc_{0.1}Ce_{0.01}Zr_{0.89}O_{1.95}$).