Characteristics of Fe-Air battery using Y_2O_3 -stabilized- ZrO_2 electrolyte with Ni-Fe electrode and $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_{3-\delta}$ electrode operated at Intermediate Temperature.

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ABSTRACT

The charge-discharge operation of a Fe-air battery using YSZ electrolyte at lower temperature was investigated using the NiFe-91 (Ni:Fe =90 :10 wt%) bimetal electrode as the fuel electrode and the $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_{3-\delta}$ (BLC) oxide electrode as the air electrode in this work. It was found that the total resistance of the cell using the NiFe-91 and BLC electrode was about 100 times smaller than that of the cell using the conventional Pt electrode, owing to its significantly small electrode resistance. It was also found that the 10 cycle charge-discharges were achieved at 600°C by using these electrodes, and the capacity of about 700 mAh/g-Fe and energy density of 600 mWh/g-Fe were also retained during 8 cycles. These results showed a significant potential; the low temperature operation of the battery using YSZ electrolyte is sufficiently possible by choosing an appropriate electrode. However, the low stability of the NiFe-91 electrode, which is due to the agglomeration, was also found in this work.

Keywords: Fe-Air battery; SORC; Solid oxide ionic conductor; YSZ

1. Introduction

Recently, the development of a rechargeable battery with high energy density has been strongly desired due to the use for storage or leveling of electric power produced from a renewable energy. As the rechargeable battery, metal-air batteries have attracted much attention due to its relatively high energy density. For example, Li-air battery has the significantly high theoretical energy density (about 10000 mWh/g) and has been widely investigated [1-6]. However, the Li-air battery has a serious problem in the reversibility of electrode reaction and its cyclability is quite poor [6]. On the other hand, Fe-air battery also has been investigated as the one of the metal-air battery by several groups [7,8]. Even though its theoretical energy density is small compared with that of Li-Air battery, Fe-air has a merit such as large natural abundance, low cost, harmless and low environmental burden. Thus far, the Fe-air battery has been mainly investigated using alkaline aqueous solution. However, in the case of this type of Fe-air battery, there remains the problem such as the decomposition of electrolyte under the charging operation or the reaction of electrolyte with CO₂ in air. Thus, this battery is considered to be used as a primary battery but not secondary battery.

Recently, a Fe-air battery using solid oxide ionic (O²⁻ ion) conductor has been proposed and demonstrated by not only the authors, but also several groups [9-17]. The operation principle of the Fe-air battery is shown in Fig. 1. The O²⁻ ion conductor is used as the electrolyte. For air electrode and fuel electrode, metal electrode and oxide electrode are used, respectively. Fe is filled in the fuel electrode side with H₂/H₂O redox mediator. The reaction in the discharge operation is as follows; O₂ at the air electrode splits into adsorbed oxygen atoms, changes into O²⁻ ion by receiving electron and is incorporated into electrolyte as O²⁻ ion. The incorporated O²⁻ ion migrates to the fuel electrode through the electrolyte, and the O²⁻ ion reacts with H₂ and H₂O is formed at the fuel electrode. After that, H₂O is regenerated as H₂ by oxidizing Fe into Fe₃O₄ at the fuel electrode side as shown in Fig. 1. In this manner, the continuous power generation can be obtained until Fe is completely oxidized into Fe₃O₄. On the other hand, the reaction in the charge operation is as follows. H₂O at the fuel electrode side is electrolyzed into H₂ and O²⁻, and H₂ produced reduces Fe₃O₄ into

Fe again. Since the operation principle of this battery is almost the same as that of the Na-S battery, this battery is expected to become the alternative to the Na-S battery and its target operation temperature also should be around 350°C. So far, it was found that the Fe-air battery using LaGaO₃ electrolyte can be operated at 500°C [12]. On the other hand, from a perspective of the practical use and cost performance, the use of ZrO₂ based electrolyte is preferable. In addition, LaGaO₃ has a disadvantage in the case of thin film electrolyte; it is difficult to reduce the thickness of LaGaO₃ electrolyte into less than 50 µm, whereas the thickness can be easily reduced into 5 µm in the case of YSZ electrolyte [13]. This is because LaGaO₃ easily reacts with Ni electrode and forms La₂NiO₄, which is not stable and leads to the delamination [17,18]. In the case of ZrO₂ based electrolyte, it has been already reported by Leonide and Landes et al. that the significant high performance of 10000 cycle charge-discharge operations could be achieved by the use of Sc₂O₃ stabilized ZrO₂ (ScSZ) based electrolyte at 800°C [14]. Besides ScSZ based electrolyte, Y₂O₃ stabilized ZrO₂ electrolyte shows relatively high oxide ion conductivity in the case of ZrO₂ based electrolyte. Even though its performance is lower than that of ScSZ based electrolyte, YSZ hardly shows rapid decrease in the oxide ionic conductivity by the phase transition at lower temperature unlike in the case of ScSZ [19,20]. Thus, YSZ electrolyte has the preferable feature for the Fe-air battery even at lower temperature.

In this work, we investigated the operation of the Fe-air battery using YSZ electrolyte with NiFe-91 bimetal (Ni:Fe = 90:10 wt%) fuel electrode and Ba_{0.6}La_{0.4}CoO_{3-δ} air electrode at 600°C because it has been reported that these electrodes showed a high performance as fuel electrode and air electrode [21,22]. Its effect on the characteristics such as the charge-discharge performance was also discussed in this work.

2. Experimental

2.1 Sample preparation

The commercial available 8mol% Y_2O_3 stabilized ZrO_2 tube (ZR-8Y, Nikkato corp.) was used for YSZ electrolyte. The dimension of the electrolyte tube was 13 mm ϕ in outer diameter, 9 mm ϕ in inner diameter and 300 mm in length. NiFe-91 (Ni:Fe = 90:10 wt%) was prepared as follows. First, the NiO powder was immersed into Fe nitrate aqueous solution at the appropriate ratio, was evaporated to dryness, and was calcined at 600°C for 6 h in air. The resultant NiO- Fe_2O_3 powder was mixed with ethyl-cellulose and a thinner, and was processed to paste. On the other hand, $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_{3-\delta}$ (BLC-64) was prepared by evaporation to dryness method; $\text{Ba}(\text{CH}_3\text{COO})_2$, $\text{La}(\text{CH}_3\text{COO})_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were solved into distilled water, were evaporated to dryness, were calcined at 400°C for 2 h, were ground and sintered at 1200°C for 6 h. The obtained $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_{3-\delta}$ powder was mixed with ethyl-cellulose and a thinner, and was processed to paste. The XRD patterns of these synthesized NiO- Fe_2O_3 and BLC-64 powder were shown in Fig. 2(a) and (b).

2.2 Experimental apparatus

The schematic illustration of the sample was shown in Fig. 3. The NiO- Fe_2O_3 paste was painted on the inside of the YSZ tube and the BLC paste was painted on the outside of the YSZ tube, and these electrodes were baked at 1000°C for 1h. In both cases, the electrode was painted several times to obtain enough electrical conduction. Especially, in the case of BLC, the electrode was painted at least 10 μm due to its lower electrical conductivity; Mizusaki et al. have reported that the electrode thickness of 10 μm is needed to obtain the enough electrical conductivity in the case of cobaltate based oxide electrode [23]. As shown in Fig. 4, it can be seen that the thickness of BLC electrode used in this work had enough thickness. In the case of the NiO- Fe_2O_3 electrode paste, the electrode was reduced to Ni-Fe bimetal at 600°C for 1 h by H_2 gas humidified at room temperature before the measurement. The Pt mesh with Pt wire was attached on the both electrode surface as a current collector. As the Fe fuel powder, a commercial available Fe_3O_4 powder (Kishida Chemical Co.,

Ltd) was set in the fuel electrode side with an alumina vessel. The loading amount was about 50 mg and the Fe_3O_4 powder was also reduced to Fe at 600°C for 1 h by H_2 gas humidified at room temperature before the measurement. Humidification of the gas was performed to suppress the strong reduction properties of hydrogen gas. This is because the dry hydrogen causes damage for the electrolyte due to its strong reduction properties.

After the reduction of the Ni-Fe electrode and Fe fuel powder, the humidified hydrogen gas was diluted with Ar gas to 10% and was sealed by the stop valves located at the upstream and downstream. Thus, the redox mediator used in this work was 10% H_2 -Ar humidified at room temperature. The charge-discharge test and impedance measurement was performed by using a potentiostat/galvanostat equipped with a frequency response analyzer (Solarton model 1287+1260, Solarton Analytical). The charge-discharge was performed by applying 5 mA (about $460\ \mu\text{Acm}^{-2}$, electrode area is about $10.7\ \text{cm}^2$) and the upper and lower limit of the charge-discharge voltage was set at 2V and 0V, respectively. The impedance measurement was performed by applying 50 mV aptitude in the frequency range from 1 M to 0.1 Hz.

3. Results and discussion

The impedance spectra of the YSZ tube cell with the NiFe-91 electrode and BLC electrode (NiFe-BLC electrode cell) were shown in Fig. 5(a). For comparison, the impedance spectra of the YSZ tube cell with the Pt electrode, which is often used as a model electrode for the electrochemical measurement at lab-scale [24-26], were also shown in Fig. 5(b). In this case, a commercial available Pt paste (TR-7902, Tanaka Kikinzoku Kogyo corp.) was painted and was fired at 1000°C for 1 h in air. It can be seen that the total impedance of the Pt electrode cell is about $1700\ \Omega$ (about $18000\ \Omega\text{cm}^2$), and that of the NiFe-BLC electrode cell was about $17\ \Omega$ (about $180\ \Omega\text{cm}^2$). That is, the total cell resistance became 100 times smaller when the electrode was changed from the Pt electrode to the NiFe-91 and BLC electrode. Especially, the total electrode resistance decreased from about $1700\ \Omega$ (about $18000\ \Omega\text{cm}^2$) to $7\ \Omega$ (about $75\ \Omega\text{cm}^2$). Thus, the electrode

resistance was significantly improved by using the NiFe-91 and BLC electrode. This small cell impedance was usually obtained when the NiFe and BLC based electrode were used. At least, 3 batteries with the similar NiFe based electrode and BLC based electrode, including a small quantity of additive to NiFe or Fe_3O_4 powder, were built and the similar performance was obtained so far. The detail and results of other batteries will be reported elsewhere in the future. The charge-discharge curves of the NiFe-BLC electrode cell were shown in Fig. 6(a). For comparison, those of the Pt electrode cell were also shown in Fig. 6(b). It can be seen that the smooth charge-discharge operation was possible by using the NiFe-91 and BLC electrode whereas the charge-discharge operation was significantly difficult due to its high cell resistivity in the case of the Pt electrode. The 10 cycle charge-discharges (ca. 100 h operation) were accomplished by using the NiFe and BLC electrode, even though YSZ was used as the electrolyte. Even though this cyclability is significantly lower than other ZrO_2 electrolyte type batteries, which were operated at around 800°C [12,14-16], this result suggested that the operation at 600°C is possible by the use of NiFe based electrode and BLC based electrode in this work. However, as can be seen in Fig. 6(a), the stable charge-discharge operation was kept during only the first 3 cycles and it immediately degraded with the cycle numbers. To clarify the reason of the degradation, the surface morphology of the NiFe-91 and BLC electrode was observed by SEM. The SEM image of the NiFe-91 and BLC electrode after the charge-discharge operation was shown in Fig. 7(b) and (d). For comparison, that of the NiFe-91 electrode after H_2 reduction and BLC electrode after baked at 1000°C was also shown in Fig. 7(a) and (c). From Figs. 7, it can be seen that the agglomeration of the NiFe-91 electrode particles occurred after the charge-discharge operation and its shape became significantly different from that after H_2 reduction, whereas that of BLC electrode was not largely change. This agglomeration is attributed to the joule heat related to electrode reaction. And in addition, since the melting point of metal electrode is typically lower than that of oxide electrode, the agglomeration of NiFe electrode became pronounced more than that of BLC. Thus, the agglomeration during the charge-discharge operation is considered as the reason for the degradation of the cyclability and the

prevention of the agglomeration will improve the cyclability.

As shown in Fig. 8, after the charge-discharge operation, the cross section of YSZ electrolyte of NiFe-91 side showed a discoloration. However, from EDX analysis, the reaction of NiFe and YSZ was not confirmed. That is, this discoloration was attributed to the blackening of YSZ by strong reduction, which might be attributed to the high cell voltage from the 7th charge operation. This result also suggests a possibility that the iron oxide powder was not sufficiently reduced from 7th cycle because the leak current occurred by this strong reduction.

The cyclability of capacity and energy density of the NiFe-BLC electrode cell was shown in Fig. 9(a) and (b). It can be seen that the capacity of about 700 mAh/g-Fe and energy density of 600 mWh/g-Fe was obtained up to the 8th cycle. This value is higher than that of the previous works using ZrO₂ electrolyte [9,12]. That is, the enough performance of this type battery using YSZ electrolyte could be obtained even at 600°C. In order to increase the cyclability, further investigations will be done to prevent the agglomeration in the near future.

Conclusion

The charge-discharge characteristics of the Fe-air battery using YSZ electrolyte were investigated using the NiFe-91 fuel electrode and BLC air electrode in this work. It was found that the total cell resistance of the NiFe-BLC electrode cell became about 100 times smaller, compared with that of the cell using the Pt electrode, owing to its significantly low electrode resistance. It was also found that the 10 cycle charge-discharges were possible at 600°C by using these electrodes and the capacity of about 700 mAh/g-Fe and energy density of 600 mWh/g-Fe were also retained during 8 cycles. However, after the charge-discharge operation, the agglomeration of NiFe-91 electrode, which leads to the degradation of the cell, was confirmed by SEM observation. It is expected that the cyclability will be further improved by preventing the agglomeration of the NiFe-91 electrode.

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Figure captions

Fig. 1 The conceptual diagram of Fe-air battery using solid oxide ionic conductor.

Fig. 2 The XRD pattern of BLC-64 and NiFe-91 electrode powder prepared: (a) BLC-64, (b) NiFe-91.

Fig. 3 The schematic illustration of Fe-Air battery using YSZ tube with NiFe-91 electrode and BLC electrode.

Fig. 4 SEM Image for the thickness of BLC electrode used in this work.

Fig. 5 Impedance spectrum of NiFe-BLC electrode cell and Pt electrode cell measured at 600°C under 10%H₂-Ar humidified at room temperature: (a) NiFe-BLC electrode cell, (b) Pt electrode cell.

Fig. 6 Charge-discharge curve of NiFe-BLC electrode cell and platinum electrode cell at 600°C:(a) NiFe-BLC electrode cell (Charge-discharge at 5 mA = 460 $\mu\text{A cm}^{-2}$), (b) Platinum electrode cell (Charge-discharge at 100 μA = 9.3 $\mu\text{A cm}^{-2}$).

Fig. 7 SEM image of NiFe-91 electrode and BLC electrode: (a) NiFe electrode after H₂ reduction, (b) NiFe electrode after the charge-discharge operation, (c) BLC electrode after baked at 1000°C, (d) BLC electrode after the charge-discharge operation.

Fig. 8 Photograph of cross section of YSZ electrolyte after the charge-discharge operation and EDX spectra of its discoloration section: (a) Photograph of the discoloration section, (b) EDX spectra of the discoloration section.

Fig. 9 Cyclability of capacity and energy density of NiFe-BLC electrode cell at 600°C: (a) capacity, (b) energy density.

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