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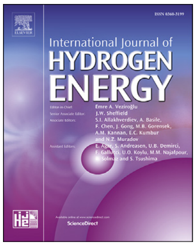

Improved performance of molten carbonate fuel cells with $(Li/Na)_2CO_3$ electrolytes by using BYS coated cathode at low operating temperatures

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ABSTRACT

In order to improve the stack life time of MCFCs, it is necessary to reduce the operating temperature of MCFCs below 600 °C, because reduced operating temperature minimizes electrolyte loss due to evaporation and corrosion. However, at the low operating temperature below 600 °C, the cell performance of MCFCs with $(Li/Na)_2CO_3$ electrolyte is too low to operate the fuel cell stack and system. In this study, we have performed wettability control of the liquid molten carbonate electrolyte by coating NiO cathodes with poor wetting property of the mixed ionic and electronic conductor (MIEC) such as BYS ($Bi_{1.5}Y_{0.3}Sm_{0.3}O_{3-\delta}$). From experiments with symmetrical cells, each polarization component with various temperatures and gas conditions were studied. To investigate effects of the BYS coated cathode on the performance of MCFCs, a 100 cm^2 single cell of MCFCs was employed. The performance of a 100 cm^2 single cell with BYS coated cathode was better than that with conventional cathode by a factor of 1.84, because BYS coated cathode reduces activation polarization and mass transfer resistance greatly.

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Introduction

Molten carbonate fuel cells (MCFCs) have been developed to produce clean and efficient power conversion with the operating temperature of 650 °C [1]. MCFCs employs molten liquid electrolytes such as $(Li/Na)_2CO_3$, $(Li/K)_2CO_3$, $(Li/Na/K)_2CO_3$ [2]. To contain the liquid between the electrodes, electrolytes are supported by a $LiAlO_2$ matrix [3]. Anode gases (H_2, CO_2, and H_2O) and cathode gases (O_2, Air and CO_2) react and carbonate ions (CO_3^{2-}) move from the cathode side to anode side. The schematic figure of MCFCs is shown in Fig. 1.

Although some products of MCFCs were introduced, there had been many barriers for commercialization. One of the most important problems of commercialization is the long-term operation capabilities of MCFCs [4]. The target of the life time of MCFCs was 40,000 h, but there were many obstacles for operation of 40,000 h [5,6]. Cell voltage of MCFCs decrease with operating time since the electrolyte in the cell was evaporated and consumed by corrosion of cell components [7].

There are many researches for enhanced long-term operations by improving stability of components such as anode, cathode, matrix, separator and current collector in operating conditions of MCFCs [8]. Decreasing the operating temperature of MCFCs provides reduced vapor pressure of electrolytes and as a result, electrolyte loss due to evaporation and corrosion can be minimized. However, operating MCFCs at the low temperature of below 600 °C reduces the performance due to the slow reaction kinetics, especially at the cathode. Consequently, a new cathode electrode for improved reaction kinetics is necessary.

In order to increase performance of MCFCs in low operating temperatures, surface-modified cathode has been investigated to improve the electrochemical characteristics of the cathode in fuel cells. For example, Ag coating on a conventional NiO cathode was employed in order to improve cell performance [9]. The Ag coating on cathode showed good catalytic activity for oxygen reduction and high electrical conductivity resulting in low charge-transfer resistance of MCFCs. Also, Song et al. [10] employed gadolinium strontium cobaltite ($Gd_{0.6}Sr_{0.4}CoO_3$, GSC), which is a mixed ionic and electronic conductor (MIEC) for intermediate temperature solid oxide fuel cells. GSC coating on MCFC cathode reduces charge-transfer resistance dramatically and improves cell performance at low temperatures (<600 °C). Nguyen et al. [11] investigated the effect of mixed ionic and electronic conductor (MIEC) coating materials with poor wetting property on cathode. Bismuth yttrium samarium oxide ($Bi_{1.5}Y_{0.3}Sm_{0.3}O_{3-\delta}$ BYS) was coated on the cathode, which has poor wetting property with the molten carbonate electrolyte. The BYS-coated cathode showed a much higher power density compared to standard cells at low operating temperatures of 550 °C with $(Li/K)_2CO_3$ electrolytes.

In addition to operate MCFCs with reduced operating temperature, Operating MCFCs with $(Li/Na)_2CO_3$ electrolytes was developed for improved long-term operation capabilities [12,13]. $(Li/Na)_2CO_3$ electrolytes shows a higher ionic conductivity, and as a result, the internal resistance of MCFCs with $(Li/Na)_2CO_3$ electrolytes are lower than that of MCFCs with $(Li/K)_2CO_3$ electrolytes [14]. Due to lower solubility ratio of NiO in $(Li/Na)_2CO_3$ electrolytes, the stability of NiO is better than that in $(Li/K)_2CO_3$ electrolytes [15]. $(Li/Na)_2CO_3$ electrolytes has advantages in the long-term operation of MCFCs [14]. For $(Li/Na)_2CO_3$ electrolytes, however, operating MCFCs was limited in the low operating temperatures of below 600 °C. It is well-known that oxygen solubility is the rate-determining step (RDS) for the reduction reaction on the cathodes of molten carbonate fuel cells in the below 600 °C [11]. Low O_2 solubility of $(Li/Na)_2CO_3$ electrolytes [16] resulted in increased mass-transfer resistance at high current densities or at low operating temperatures of below °C. Therefore, large cathode polarization due to the low O_2 solubility should be overcome to use the $(Li/Na)_2CO_3$ electrolyte for the reduced temperature MCFCs (<600 °C).

In this study, MIEC-coated cathode with poor wetting property proposed by Nguyen et al. [11] was introduced in order to reduce operating temperatures of MCFCs with $(Li/Na)_2CO_3$ electrolytes. The target operating temperature of MCFCs with $(Li/Na)_2CO_3$ electrolytes is set to 550 °C. The effect of MIEC-coated cathode with poor wetting property on the performance of MCFCs was investigated. First, the wetting property of BYS-coated cathode with $(Li/Na)_2CO_3$ electrolytes was investigated. Next, the reason of the low performance at

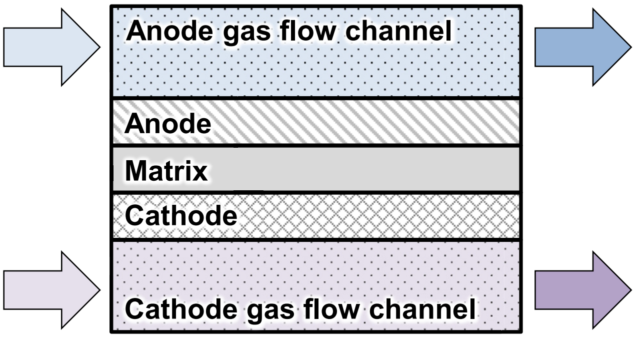


Fig. 1 – Schematic figure of MCFCs.

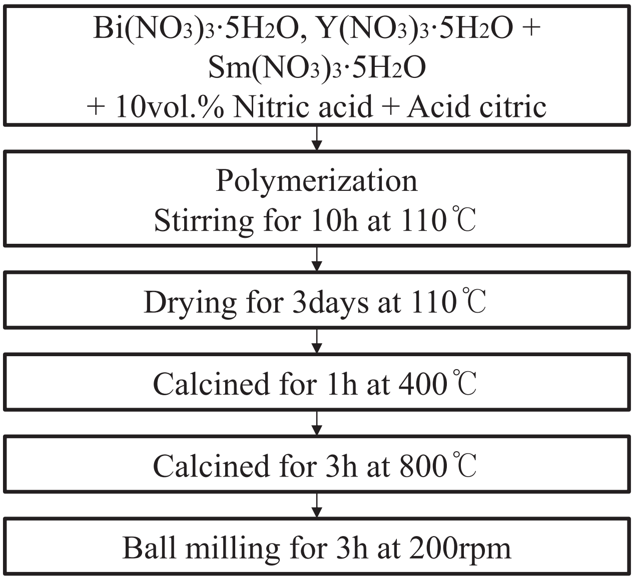


Fig. 2 – Fabrication process of BYS particles.

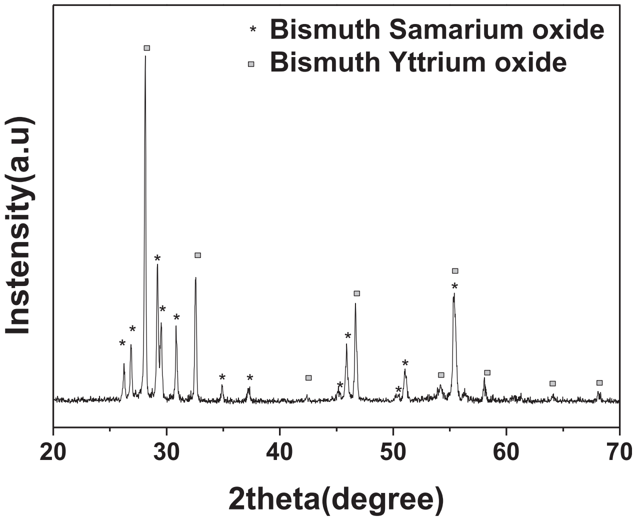


Fig. 3 – XRD results of fabricated BYS powders sintered at 800 °C for 3 h [11].

low temperature with $(Li/Na)_2CO_3$ electrolytes was studied with anode and cathode symmetrical cells. Reaction orders and activation energies at various conditions were measured. The polarization components of the conventional NiO cathode were compared with those of the BYS-coated cathode. Finally, effects of the BYS-coated cathode were investigated by the operation of 100 cm^2 single cells at various temperatures (<600 °C). BYS-coated cathode improves the performance of the cell dramatically at the low temperatures by decreasing both charge-transfer and mass-transfer resistances.

Wettability control of cathode using BYS particles

Fabrication process of BYS

Nguyen et al. [11] studied the effect of the Bismuth, Yttrium, and Samarium oxide materials on the performance of MCFCs $(Li/K)_2CO_3$ electrolytes. Among many candidates such as BSO, BYO, Bi_2O_3, and BYS, BYS-coated cathode showed the best cell performance. In this work, BYS (Bismuth yttrium samarium oxide, $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$) was selected as an example of MIEC, because BYS showed best performance in the previous work [11]. BYS particles were fabricated using the citrate method [17]. Fabrication process of BYS particles were presented in Fig. 2. After fabrication process, dried powder was crushed by mortar and pestle. After that, uniform particle size of 1–2 um was obtained.

Fig. 3 shows the X-ray diffraction (XRD, Rint/DMAX-2000, Rigaku) results of fabricated BYS particles [11]. In BYS particles, two types of main phases such as BSO (Bismuth samarium oxide) and BYO (Bismuth yttrium oxide) were identified. These results revealed successful material fabrication of BYS powders.

Wetting characteristics of BYS-coated cathode

For uniform coating of BYS on the cathode, spraying method [18] was employed. The coating process was repeated until all BYS solution infiltrated the porous cathode with the 9.5 wt%, because with a BYS loading amount of 9.5 wt% showed the

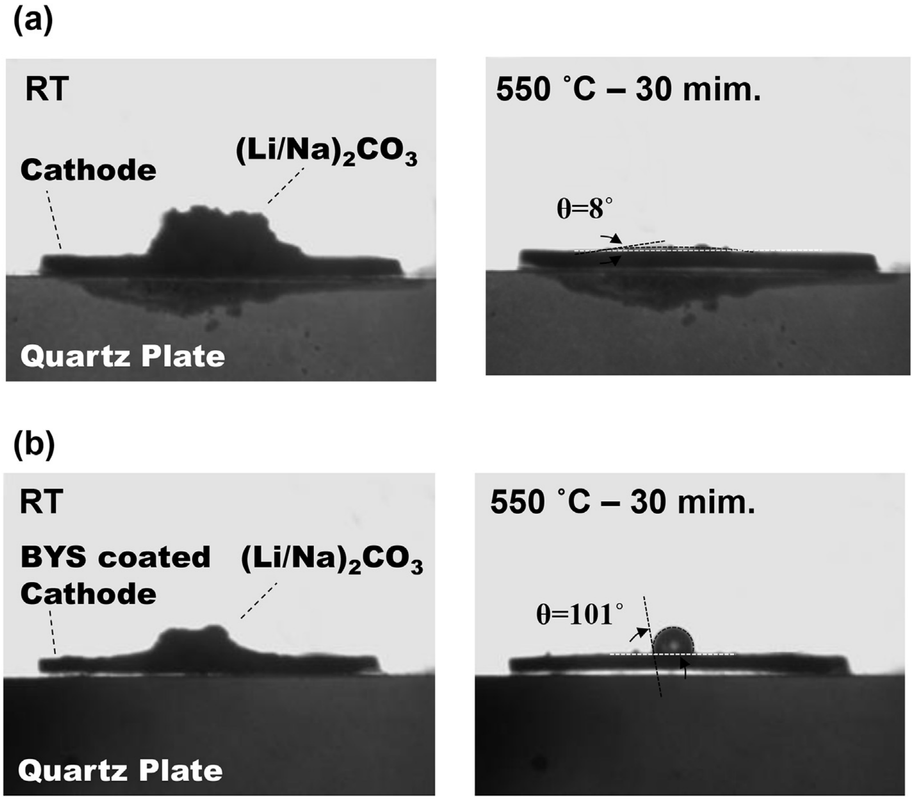
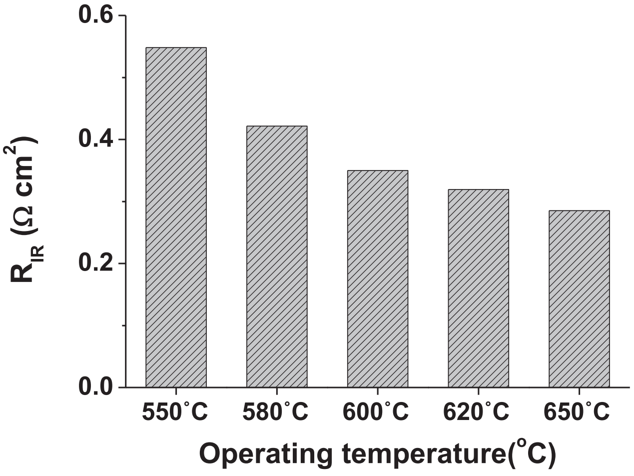


Fig. 4 – Wetting properties of $(Li/Na)_2CO_3$ on cathode: (a) conventional NiO cathode and (b) BYS coated NiO cathode.

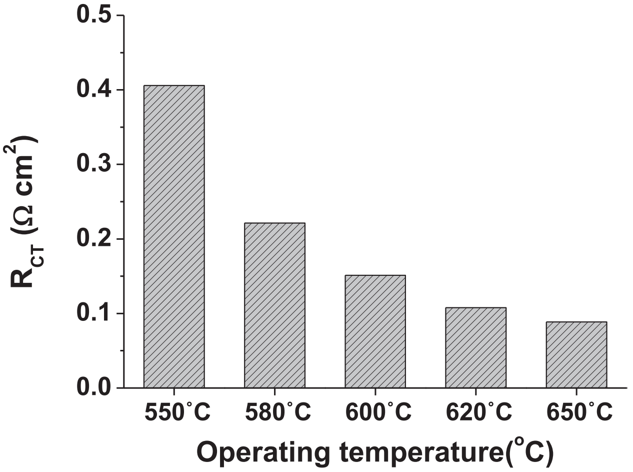
highest power densities at 550 °C in the previous work [11]. The coating process was conducted on the sintered Ni cathode. After that, the wetting characteristics of BYS coated cathode was investigated using the contact angle analyzer (Phoenix 300). Before measuring wetting angle of the coated cathode, sintered Ni cathode was oxidized in the cathode atmosphere (Air:CO_2 = 70:30) at 600 °C. After that, $(Li/Na)_2CO_3$ electrolyte powders were on the NiO cathode. Finally, the chamber was heated up to 550 °C which is the target operating temperature in the cathode atmosphere (Air:CO_2 = 70:30). After holding 30 min at 550 °C, the contact angle of the cathode was measured. Fig. 4 presents the results of the contact angle measurements for the conventional cathode and the BYS coated cathode. In the case of the conventional cathode, the process was identical.

The contact angle of the BYS coated cathode with $(Li/Na)_2CO_3$ electrolytes at 550 °C was 101°. The BYS coated cathode showed very poor wetting property. Meanwhile the contact angle of the conventional cathode is 8°. It showed very good wettability. Thus, when poor wetting materials were coated on the cathode, more cathode surface could be exposed to the gas phases of cathode reactants, which reduced the electrolyte film thickness and made the other reaction path way through the BYS, resulting in a reduction in the mass transfer resistance.

(a) Internal resistance (R_{IR})



(b) Charge transfer resistance (R_{CT})



(c) Mass transfer resistance (R_{MT})

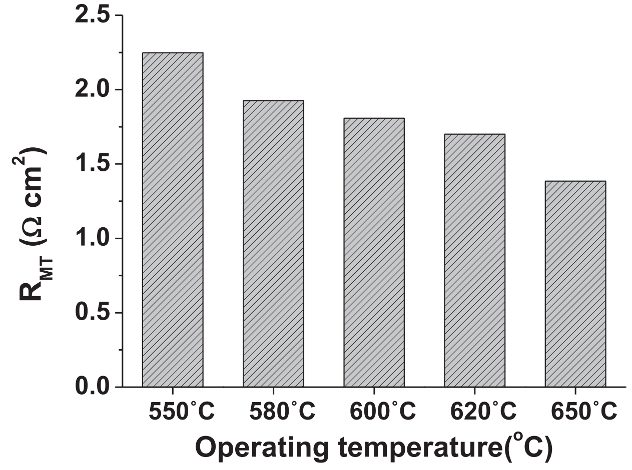


Fig. 5 – Distribution of anode polarization components with respect to temperature: (a) Internal resistance, (b) charge-transfer resistance, and (c) mass-transfer resistance.

Analysis of polarization components using symmetrical cell

Anode polarization components

Anode and cathode symmetrical cells for MCFCs were operated to separate the anode side polarization and cathode side polarization. From an electrochemical impedance spectroscopy (EIS) analysis [19], each polarization components such as internal resistance (R_{IR}), charge-transfer resistance (R_{CT}), and mass-transfer resistance (R_{MT}) was obtained by the equivalent circuit. EIS was measured at open circuit voltage (OCV) using Solatron S1287 and 1255B with the frequency range from 10^4 Hz to 10^{-2} Hz. Nyquist plots obtained from the EIS analysis of the MCFCs have an intercept on the real axis indicating an ohmic resistance (R_{IR}). The EIS results are also indicated by two semi-circles at high frequency ranges (500 Hz–50 Hz) and low-frequency (<1 Hz) ranges, representing the resistance related to electrochemical reactions, or charge-transfer resistance (R_{CT}) and mass-transfer resistance (R_{MT}), respectively.

First, an anode symmetrical cell with $(Li/Na)_2CO_3$ electrolyte was investigated at various operating temperatures (650 °C, 620 °C, 600 °C, 580 °C, and 550 °C) in order to investigate the operating temperature on the polarization components. The size of the active area for the anode symmetric cell is 25 cm^2. A Ni - 5wt% Al anode and γ-$LiAlO_2$ matrices were used. For electrolytes, a tape-casted $(Li/Na)_2CO_3$ electrolyte was used. The sealing pressure is 0.2 MPa. Anode gases are composed of H_2, CO_2, and H_2O with the compositions of 0.72: 0.8: 0.1. The gas utilization for the anode side (H_2) and the cathode side (O_2 and CO_2) were fixed to 0.4 at 150 mA/cm^2. It means 40% of gases are consumed to electrochemical reaction at 150 mA/cm^2.

Fig. 5 (a) presents the distribution of internal resistance of the anode symmetrical cell at various temperatures. At 650 °C, values of R_{IR}, R_{CT}, and R_{MT} are 2.85 Ωcm^2, 0.89 Ωcm^2, and 13.85 Ωcm^2, respectively. At 550 °C, values of R_{IR}, R_{CT}, and R_{MT} are 5.48 Ωcm^2, 4.06 Ωcm^2, and 22.48 Ωcm^2, respectively. R_{IR}, R_{CT}, and R_{MT} increased by 92.1%, 357.8%, and 62.3%, respectively, at 550 °C comparing with that at 650 °C. In the anode symmetrical cell, R_{CT} was the most influenced by the operating temperature. The compositions of R_{CT} and R_{MT} at 550 °C are 12.68% and 70.21% of the total polarization. R_{MT}, which had the largest compositions in the total polarizations, did not largely influenced by the temperature. It can be inferred that the anode polarization terms has little effect on the low performance of MCFCs at 550 °C.

Cathode polarization components

A cathode symmetrical cell with $(Li/Na)_2CO_3$ electrolyte was investigated at various operating temperatures (650 °C, 620 °C, 580 °C, and 550 °C). The size of the active area and experimental conditions were the same with the anode symmetrical cell. Cathode gases were composed of Air and CO_2 with the compositions of 0.7: 0.3. The gas utilization of CO_2 was 0.4. By comparing effects of the BYS coated cell on the performance, the cathode symmetrical cell with the conventional NiO cathode and the BYS coated NiO cathode.

EIS results of the conventional cathode and the BYS-coated cathode are presented in Fig. 6(a) and (b). Right circles of the EIS result for the symmetrical cell with conventional cathode increases drastically as the operating temperature decreases. However, in the EIS results of the symmetrical cell with the BYS-coated cathode, the second semi-circle increases little. From these EIS results, polarization components of the conventional cathode and the BYS coated cathode were obtained.

Fig. 7 presents the distribution of internal resistance of the cathode symmetrical cell at various temperatures. R_{IR}, R_{CT}, and R_{MT} increased by 36.67%, 302.56%, and 845.59%, respectively, at 550 °C comparing with that at 650 °C, when the conventional NiO cathode was employed in the symmetrical cell. R_{IR}, R_{CT}, and R_{MT} increased by 33.84%, 265.01%, and 404.25%, respectively, at 550 °C comparing with that at 650 °C, when the BYS coated cathode was employed. By decreasing temperature from 650 °C to 550 °C, R_{MT} of the cathode side was increased abruptly due to the low oxygen solubility of $(Li/Na)_2CO_3$ electrolytes.

Polarizations of the conventional cathode were compared with those of the BYS coated cathode. R_{IR} of the BYS-coated cathode is slightly higher than that of the conventional cathode. Differences of R_{IR} between the conventional cathode and the BYS coated cathode were less than 0.01 Ωcm^2. Effect of these differences was quite small. However, R_{CT} and R_{MT} of the conventional cathode are significantly higher than those of the BYS-coated cathode. At 550 °C, the difference of R_{MT} between the conventional cathode and the BYS-coated cathode is 32.25 Ωcm^2. R_{MT} of the conventional cathode is 2.34 times higher than that of the BYS-coated cathode. The total polarization of the conventional cathode is 2.09 times higher than that of the BYS-coated cathode due to the increased R_{MT}.

From these results, it was found that the low operating temperature results in dramatically increased R_{MT} in the cathode side. The low performance of MCFCs with $(Li/Na)_2CO_3$ electrolytes was come from the increased R_{MT} of the cathode side. Comparing with the conventional cathode, BYS-coated cathode showed lower mass-transfer resistance at 550 °C than the conventional cathode. Decreased R_{CT} and R_{MT} of the BYS-coated cathode would result in the enhanced performance of MCFCs.

Activation energy of cathode polarization components

In the previous experiment with the BYS-coated cathode and $(Li/Na)_2CO_3$ electrolytes, there is no effect of gas-phase diffusion in the cathode [11]. For the detailed investigation into the effect of the BYS-coated cathode on $(Li/Na)_2CO_3$ electrolytes, gas composition and temperature dependencies of the polarization components were investigated.

Fig. 8 shows the gas composition dependency to R_{CT} of the cathode side at different temperatures for the conventional cathode and the BYS-coated cathode. Both in the partial pressure dependency of O_2 and CO_2, R_{CT} of the BYS-coated cathode showed smaller values than the conventional cathode at a certain temperature and a gas partial pressure. Decreased values of R_{CT} was came from the increased reaction site of the BYS-coated cathode [9].

R_{CT} decreased as the pO_2 (partial pressure of O_2) increased. The slope of the curve in Fig. 8(a) is slightly different from the

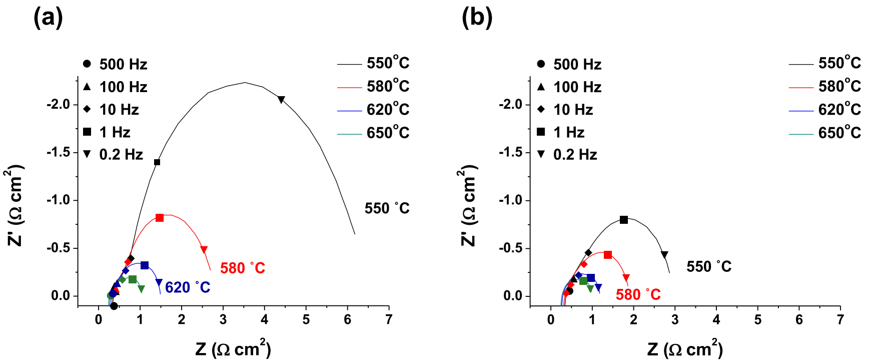
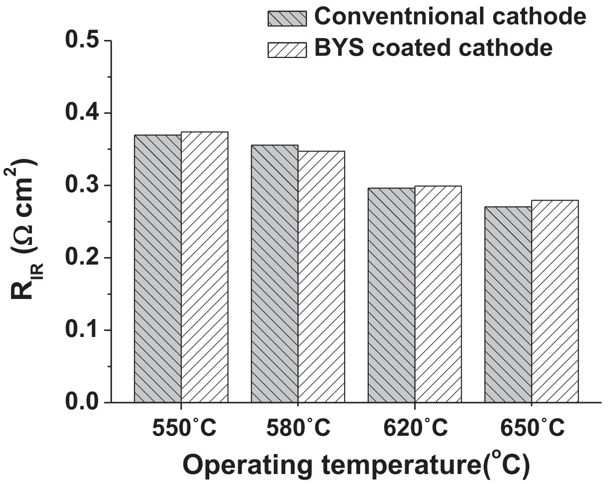


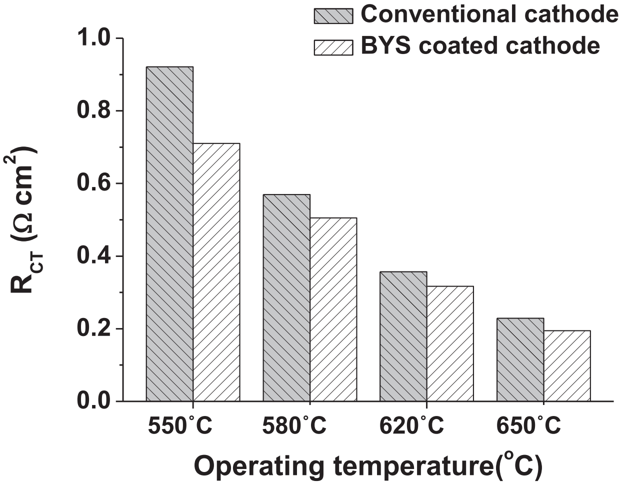
Fig. 6 – EIS results of cathode symmetrical cell using (a) conventional cathode and (b) BYS coated cathode.

slope of the curve in Fig. 8(b). BYS-coated cathode decreases the value of R_{CT} and was not influenced by the dependency of the gas partial pressure. The slope of the polarization - partial pressure graph means the reaction mechanism. With the variation of pO_2, the variation of pCO_2 does not influence the slope of the graph. BYS-coated cathode does not influence the reaction of the reaction mechanisms of the cathode side.

(a) Internal resistance (R_{IR})



(b) Charge transfer resistance (R_{CT})



(c) Mass transfer resistance (R_{MT})

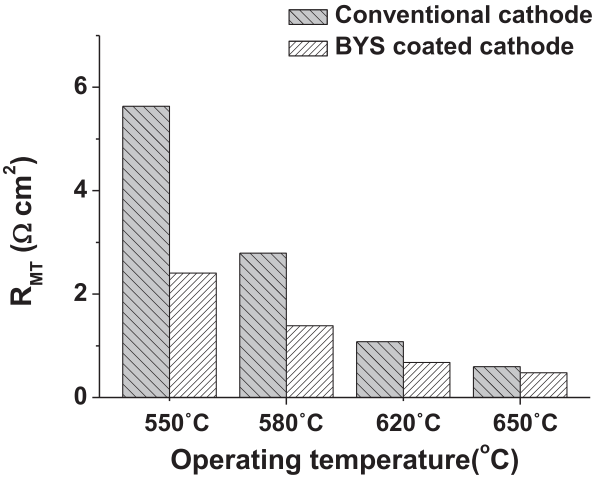


Fig. 7 – Distribution of cathode polarization components with respect to temperature: (a) Internal resistance, (b) charge transfer resistance, and (c) mass transfer resistance.

Fig. 9 presents the gas composition dependencies to R_{MT} of the cathode side at different temperatures. As shown in Fig. 9(a) and (b), the polarization component of R_{MT} decreases by employing BYS coated cathode at a certain temperature. In addition to the value of R_{MT}, the slopes of the curve in Fig. 9 (a) and (b) were influenced by the BYS-coated cathode. As pO_2 decreases, R_{MT} increases. It means that the slope of the graph is negative. At 550 °C, the slopes of the curve with the BYS-coated cathode and the conventional cathode are −0.302 and −0.556, respectively. When the BYS coated cathode was employed in MCFCs, the reaction order was increased. It means that the polarization of R_{MT} does not increase drastically at the low pO_2. The difference of the R_{MT} with different temperatures was smaller than the conventional cathode at a certain pO_2 when the BYS coated cathode was employed.

Fig. 9(c) and (d) is shows the effect of the pCO_2 on R_{MT}. In the symmetrical cell with the conventional cathode shown in Fig. 9(d), the slope of the curve at 650 °C and 620 °C is negative. However, At 550 °C and 580 °C, the slope of the curve is positive. In those temperature below 580 °C, as pCO_2 decreases, the mass transfer resistance decreases also. The slope of the graph is negative at the temperature ranges of 550 °C–650 °C. R_{MT} of the BYS coated cathode is smaller than that of the conventional cathode when the BYS coated cathode was employed.

Activation energies of R_{CT} and R_{MT} of the conventional cathode are 95.05 kJ/mol and 200.11 kJ/mol, respectively in the conventional operating condition of 15% O_2 + 30% CO_2 + 55% N_2. However, the activation energies of R_{CT} and R_{MT} of BYS-coated cathode is 36.13 kJ/mol and 115.54 kJ/mol, respectively. Activation energies were decreased by 61.99% in R_{CT} and 42.2% in R_{MT}. In the gas conditions of 30% O_2 + 30% CO_2 + 40% N_2, activation energies of R_{CT} and R_{MT} of BYS-coated cathode is smaller than activation energies of conventional cathode. Also, when the partial pressure of O_2 increases, the activation energy of R_{CT} and R_{MT} was decreased. Decreased activation energies means that the polarization component is less sensitive to temperature and that the performance of the fuel cell was improved at low temperature.

Application of BYS-coated cathode to 100 cm^2 single cell of MCFCs

Experimental set-up

Effects of poor wettability of the MIEC coating on the performance of MCFCs were investigated from 100 cm^2 single cell tests. Fig. 1(a) shows the anode and cathode side cell frame of 100 cm^2 single cell. In the single cell operation, Ni-5wt% Al anode, BYS coated NiO cathode, γ-$LiAlO_2$ matrix were used. A tape-casted (52/48) mol % Li_2CO_3/Na_2CO_3 electrolyte was used. The operating pressure is 1 atm. The sealing pressure of

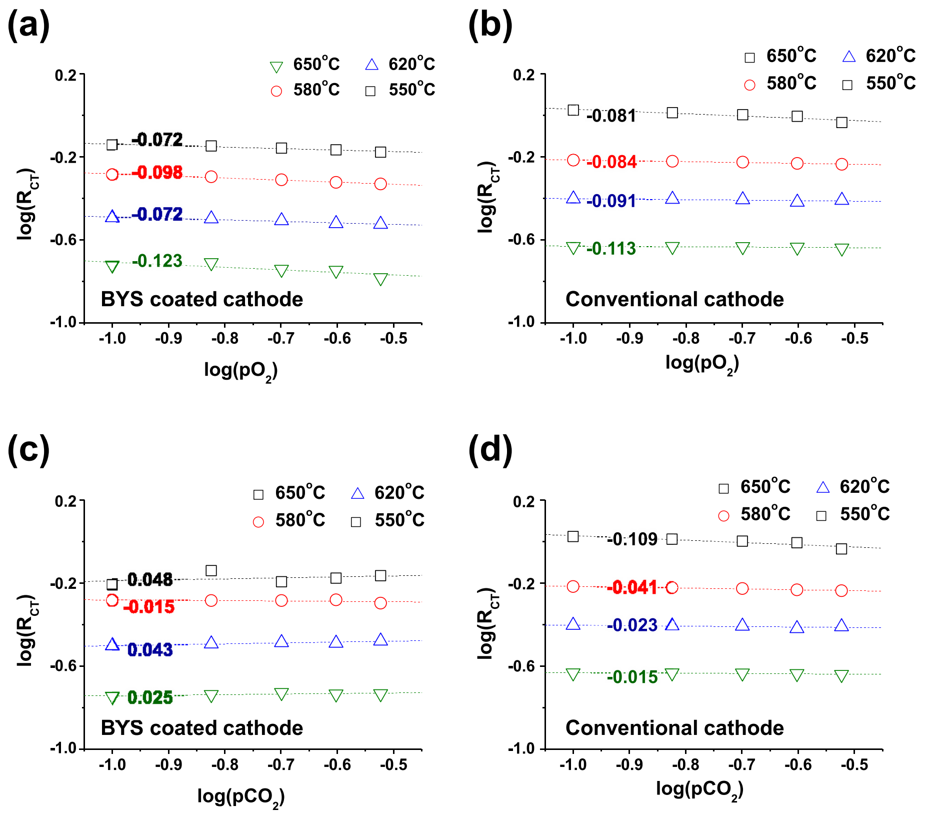


Fig. 8 – Gas composition dependency to the charge transfer resistance (R_{CT}) at different temperature (a) O_2 dependency of the BYS coated cathode, (b) O_2 dependency of the conventional cathode, (c) CO_2 dependency of the BYS coated cathode, and (d) CO_2 dependency of the conventional cathode.

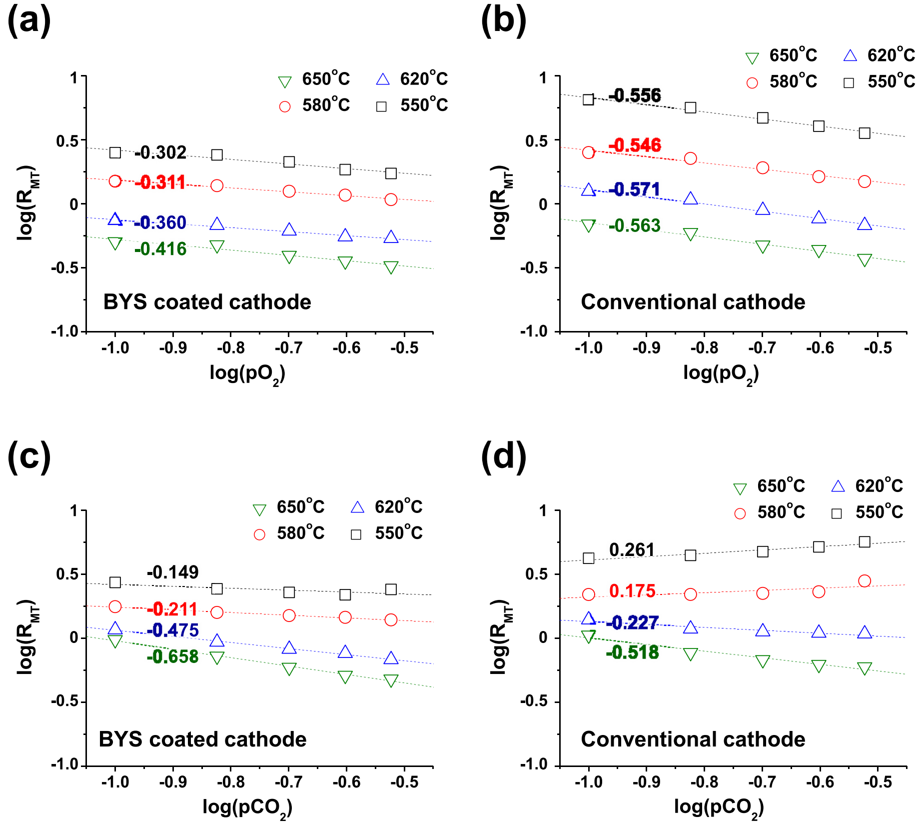


Fig. 9 – Gas composition dependency to the mass transfer resistance (R_{MT}) at different temperature (a) O_2 dependency of the BYS coated cathode, (b) O_2 dependency of the conventional cathode, (c) CO_2 dependency of the BYS coated cathode, and (d) CO_2 dependency of the conventional cathode.

Table 1 – 100 cm^2 single cell operating conditions.

Temperature		650 °C
Pressure		1 atm
Sealing Pressure		0.2 MPa
Gas utilization (Anode H_2/ cathode O_2 and CO_2)		0.4 at 150 mA/cm^2
Anode		Ni + Ni-5%Al
Cathode		Lithiated NiO/BYS coated NiO
Matrix		γ-$LiAlO_2$
Electrolyte		(52 + 48) mol% $(Li + Na)_2CO_3$
Gas flow rate	Anode	357 sccm
	Cathode	952 sccm
Gas Composition	Anode	$H_2:CO_2:H_2O = 0.72:0.18:0.1$
	Cathode	$Air:CO_2 = 0.7:0.3$

0.2 MPa was applied to the cell frame. The gas utilization for the anode side (H_2) and the cathode side (O_2 and CO_2) were fixed to 0.4 at 150 mA/cm^2. The gas compositions are $H_2/CO_2/H_2O$ = 72:18:10 for the anode gas and Air/CO_2 = 70:30 for the cathode gas. Experimental conditions are summarized in Table 1. The performance of the cells were compared at the operating temperatures of 650 °C, 620 °C, 580 °C and 550 °C.

Fig. 10 (a) presents 100 cm^2 Single cell frames for the anode side and the cathode side. Fig. 10(b) presents conventional NiO cathode. Fig. 10(c) presents the 5.9 wt % BYS coated cathode. On the surface of the Ni back bone, BYS particles were placed after BYS coating. For comparison, the 100 cm^2 single cell with conventional NiO cathode and the BYS-coated cathode were conducted.

Comparison of the performance of 100 cm^2 single cell

The performance of the 100 cm^2 single cell for MCFCs with respect to the operating temperature is summarized in Table 2. Experiments were repeated 3 times and the voltage difference in experiments at 150 mA/cm^2 was less than 5 mV, which is less than 1% of the cell voltage at 150 mA/cm^2. Fig. 11 presents I-V characteristics of the 100 cm^2 single cell with the conventional NiO cathode and the BYS coated cathode. At 650 °C and 620 °C, cell voltage at 150 mA/cm^2 of the single cell with the conventional cathode is slightly better than that of the single cell with the BYS-coated cathode. Voltage differences at 150 mA/cm^2 are 15 mV at 650 °C and 18 mV at 620 °C.

However, when the operating temperature is lower than 600 °C, the performance of the single cell with BYS-coated cathode is better than that of the single cell with the conventional cathode. As shown in Fig. 11, as the current density of the cell increases, the voltage of the cell with conventional NiO cathode decreased sharply due to the mass transfer resistance. The single cell with the conventional cathode is

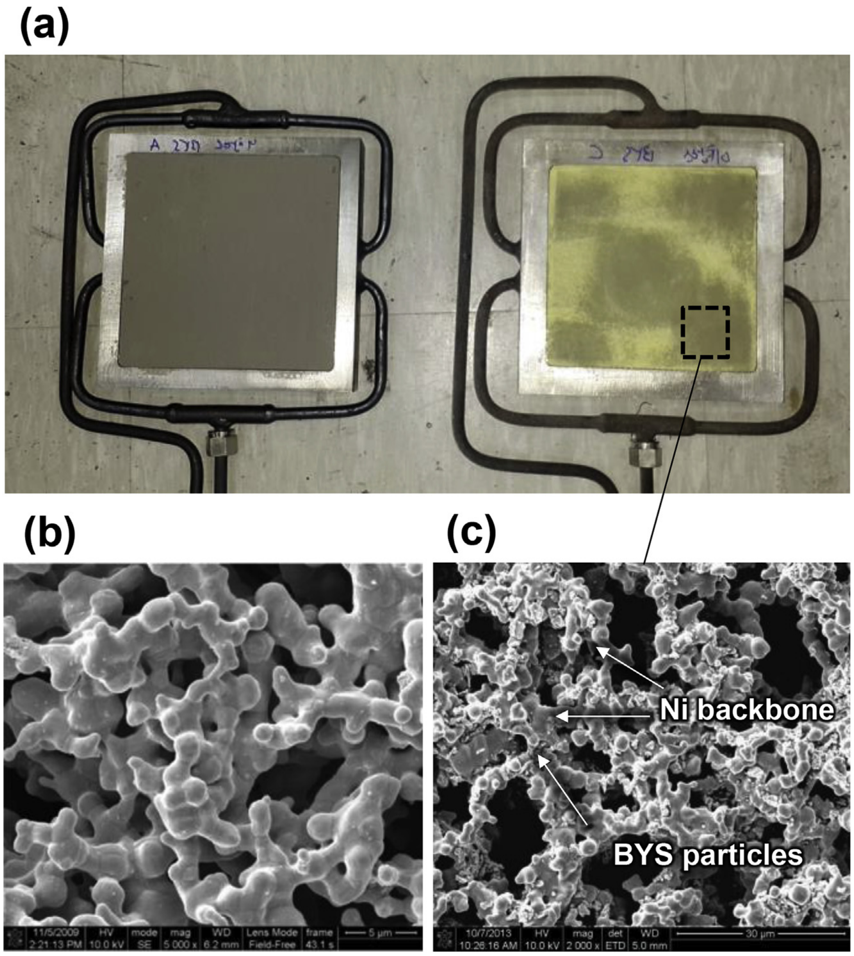


Fig. 10 – 100 cm^2 Single cell frame and BYS coated cathode.

Table 2 – Performance of 100 cm^2 single cell with respect to operating temperatures.

Temperature	650 °C		620 °C		580 °C		550 °C	
Cell type	As is	BYS coated	As is	BYS coated	As is	BYS coated	As is	BYS coated
Cell voltage (V) at 150 mA/cm^2	0.843	0.828	0.804	0.786	0.611	0.672	–	0.501
Maximum power density (mW/cm^2)	168.7	165.7	146.4	139	91.7	101.2	40.0	73.7

not possible to operate at 150 mA/cm^2 and 550 °C, the single cell with BYS-coated cathode shows 0.501 V at 150 mA/cm^2. In order to secure long-term operation capability of BYS-coated cell, the cell was operated at 550 °C for 1000 h. Significant performance degradation was not observed.

Power density curves of 100 cm^2 single cell using the conventional cathode and the BYS-coated cathode at 650 °C and 550 °C are presented in Fig. 12. At 650 °C, two power density curves show similar tendency. Maximum power densities were observed at 250 mA/cm^2. Difference of the maximum power density is 3 mW/cm^2. However, power density curves at 550 °C showed different tendencies. A single cell with BYS-coated cathode and conventional NiO cathode showed maximum power density 73.68 mW/cm^2 at 120 mA/cm^2 and 40.04 mW/cm^2 at 70 mA/cm^2. BYS-coated cells showed a much higher power density compared to the single cell with the conventional cathode, with a factor of 1.84 at the low operating temperature of 550 °C. BYS coated cathode improves the performance of MCFCs at low temperature.

Discussion

Especially at low operating temperature below 600 °C, slow O_2 dissolution kinetics results in low cell performance of MCFCs with Li/Na electrolyte. Because oxygen solubility is the rate determining step, the wetting property of the cathode has a significant effect on the performance of MCFCs.

The reaction pathways with respect to the wetting property of cathode were investigated. Fig. 13(a) presents the reaction pathways of the conventional NiO cathode showing good wetting property. Electrolyte film (molten carbonates) covers the cathode and the covered region became inactive areas due to the low solubility of O_2. As a result, the cathode with good wetting property results in high mass-transfer resistance and high activation energy at the low operating temperature.

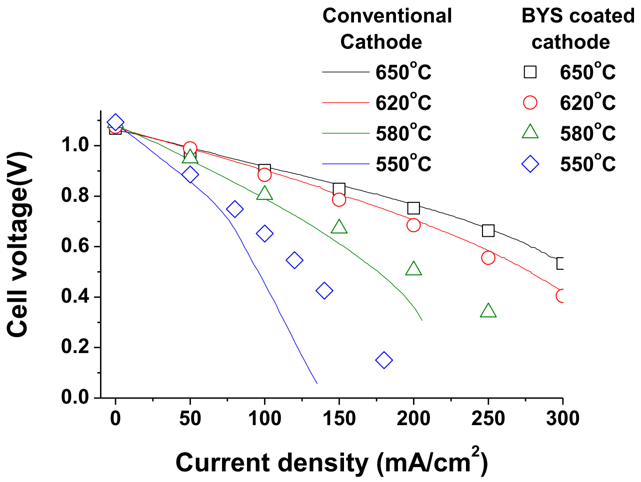


Fig. 11 – IV curves at different temperatures of 100 cm^2 single cell using conventional cathode and BYS coated cathode.

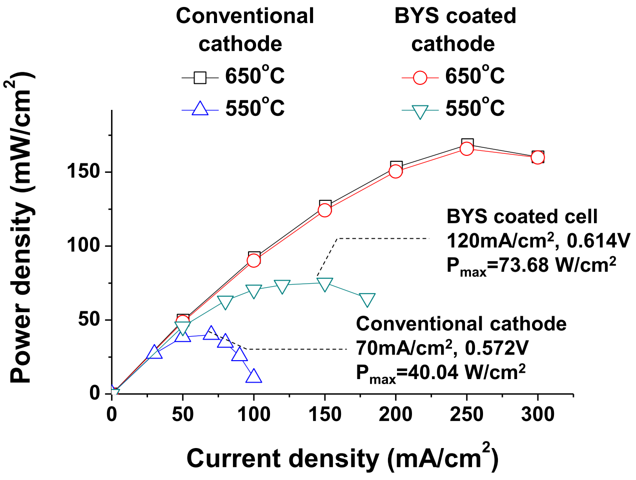


Fig. 12 – Power density curves of 100 cm^2 single cell using conventional cathode and BYS coated cathode.

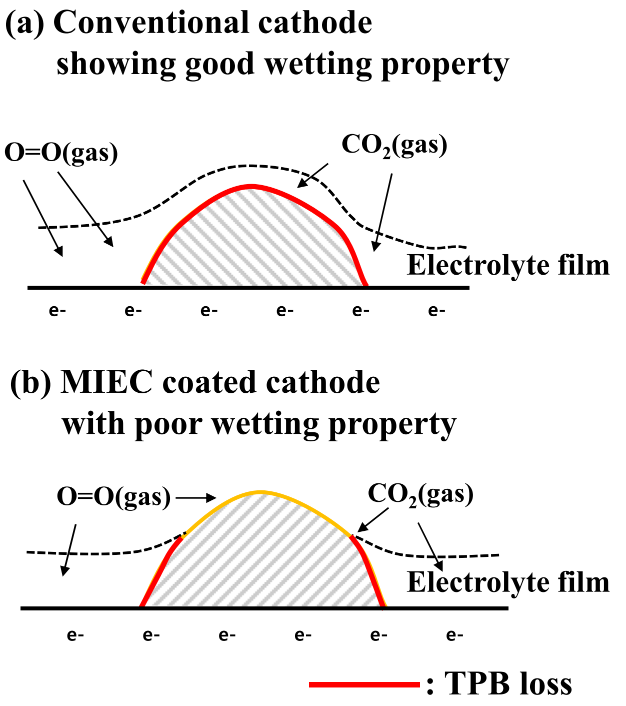


Fig. 13 – Mechanism of MIEC with poor wetting property.

Fig. 13(b) presents the reaction pathways of MIEC coated cathode. Due to the MIEC coating, the cathode surface shows poor wetting with the liquid electrolyte. The bare surface of BYS can adsorb oxygen molecules and then form oxygen ions like a SOFC cathode reactions. Finally, the oxygen ions can diffuse to the interface between electrolyte and BYS where carbonate ions can be produced. As a result, the performance of BYS-coated cathode cell increased dramatically because oxygen ions diffusing through the BYS are faster than oxygen molecule dissolution into the electrolyte especially at the low operating temperature of 550 °C. Finally, the mass-transfer resistance of the BYS-coated cathode and the charge-transfer resistance decreased at the low operating temperature and, as a result, the performance was improved dramatically.

Conclusion

In this work, the effect of the BYS coated cathode which is one of MIEC materials with poor wetting property on the performance of MCFCS with $(Li/Na)_2CO_3$ electrolytes at low operating temperatures. The contact angle of the BYS coated cathode at 550 °C and cathode atmosphere is 109°, while the contact angle of the conventional cathode is 9°. Poor wetting property of BYS coating on cathode increases reaction site such as triple phase boundary by making electrolyte film thinner. As a result, oxygen ions can diffuse to reaction site and oxygen absorption, dissociation and O^{2-} transport were enhanced.

From the experiments with symmetrical cells with BYS coated cathode and conventional cathode, the effect of the BYS coated cathode on polarization terms were studied. Mass transfer resistance was decreased by 57.3% by employing the BYS coated cathode. Additionally, charge transfer resistance was decreased by 22.88%. Decreased charge transfer and mass transfer resistance of the BYS coated cathode resulted in the enhanced performance of MCFCs. In 100 cm^2 single cells of MCFCs at 550 °C, the maximum power density with the BYS coated cathode was 73.68 mW/cm^2 and increased by 1.84 times of comparing with the maximum power density with the conventional cathode. BYS coated cathode enables the operation of MCFCs with $(Li/Na)_2CO_3$ electrolytes at low operating temperatures. It will provide long-term operation stability to components of MCFCs.

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