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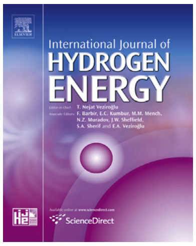

Effects of vibrations in marine environments on performance of molten-carbonate fuel cells

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ABSTRACT

Owing to the strengthening of environmental regulations, highly efficient and environmentally sustainable power supply systems have attracted significant attention as auxiliary power units (APUs) for marine applications. Among several candidates, molten carbonate fuel cells (MCFCs) is of particularly interest because it provides high efficiency with essentially no greenhouse gas emissions of NO_x and SO_x. In this study, the effects of vibrations caused by sea-waves and swells on the operation of MCFCs on marine ships are investigated. An MCFC single cell with a unit area of 100 cm^2 was tested in a vibration environment at an operating temperature of 620 °C. At a low sealing pressure (0.1 MPa), the performance of the cell decreased owing to increased mass-transfer resistance. Electrochemical impedance spectroscopy revealed that using oxygen and CO_2 as the cathode reactants mitigates the degradation by the vibration induced mass-transfer resistance. In addition, the MCFC single cell is operated under various vibration conditions, including the resonance frequency (13 and 29 Hz). It was found that the vibration environment does not affect the performance of MCFCs under normal operating conditions.

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Introduction

Marine transport contributes 14% of the NO_x and 16% of the SO_x of total emissions [1]. Marine industries strive toward reducing NO_x and SO_x emissions. Fuel cells employed as auxiliary power units (APUs) are recently considered as possible solutions to significantly reduce the emission of air pollutants [2]. Fuel cells provide many advantages, such as high-efficiency ($\leq$60%), silent electricity generation, and low emissions [3].

For marine applications, the molten-carbonate fuel cell (MCFC) is considered one of the most promising fuel-cell technologies. MCFCs provide several advantages over diesel engines, such as low emission levels, high efficiency, and silent, vibration-free electricity generation. MCFCs convert the chemical energy of fuels directly and efficiently into electricity via electrochemical reactions [4]. They operate with a high tolerance to air contamination and carbon monoxide at a high temperature. Moreover, MCFCs do not require moving parts, making their operation quiet and vibration-free; expensive enclosures and noise-reduction measures are not needed [5].

It is necessary to investigate the operation of MCFCs in marine environments for the application of MCFCs for APUs. In marine environments, seawater mists can be introduced into the cathode side [6]. Several studies showed that impurities from the sea atmosphere negatively affect the performance of MCFCs [7–12]. Watanabe et al. reported that the SO_4^{2-} impurity in seawater produces a negative effect on the cell performance [7]. Whereas, Song et al. investigated the effects of impurities such as NaCl in a marine atmosphere reporting that Na^+ ions improved the cell performance slightly and that the emitted HCl did not cause severe corrosion [6,13]. According to the previous works, moreover, elements such as Mg^{2+}, Ca^{2+}, K^+, and CO_3^{2-} impurities added into the reactant gas produced no negative effects on the cell performance of MCFC stacks [14].

In addition to the effect of chemicals from seawater mists, mechanical factors in marine environments, *i.e.* vibration due to wind-waves and swells [15], affecting the performance of MCFC stack and the cell frame of MCFC should be considered for the marine applications [16]. For example, the matrix could easily be deformed as it existed as molten paste under the operating conditions [17]. The performance of MCFCs would also be degraded if the cell components are damaged due to continuous vibration. If the matrices and wet-seal are creaked by the mechanical vibrations, the oxidant gas passes through the matrix from the cathode to the anode, or fuel cross-over [17], resulting in performance degradation and eventually the direct combustion of the hydrogen fuels with the oxygen leaked. In the case, the performance of the fuel cell rapidly decreases including the cell temperature rise and electrolyte evaporation [18]. Studies on the influence of vibration on MCFCs are therefore necessary for long-term and stable operation of MCFCs in marine environments.

In this work, we confirmed the MCFCs performance and physical durability for the application of MCFCs in marine industries. The MCFC performance was investigation using the single cells with a unit area of 100 cm^2 operated under various vibration conditions similar with real marine environments. The vibration system was constructed with two hydraulic cylinders in order to simulate vibration environments. The vibration effects were studied using MCFC single cells under different sealing pressures. Electrochemical impedance spectroscopy (EIS) was employed to distinguish the factors causing performance degradation of MCFC by the vibrations [19]. Finally, the cell durability was examined in longer time operations under continuous vibrations at a resonance frequency, where the resonance frequency of single cells was obtained by vibration frequency sweep analysis.

Operation of MCFC single cell in vibration environment

MCFC single cell and operating conditions

An MCFC single cell is composed of the anode, cathode, matrices, two current collectors, electrolyte sheets, and two metallic cell frames, as shown in Fig. 1. Ni-5wt%Al anode, lithiated NiO cathode, and γ-$LiAlO_2$ matrices were used. For the electrolyte sheet, a mixture of Li_2CO_3 and K_2CO_3 was used. AISI 316L was used for the cell frame and the cathode current collector. A Ni plate was used for the anode current collector. Using a mass-flow controller (MFC), the volume-flow rate of reactant gases was controlled. The current density of the MCFC single cell was measured at various cell voltages swept by a voltage meter at cell operation temperature of 620 °C. The gas compositions are summarized in Table 1. The values of the gas utilization for the anode and cathode gas were fixed to 0.4.

In the operation of MCFCs, different sealing pressures, staking pressure, and contact pressure were applied to a cell by which the contact resistance between the electrodes and

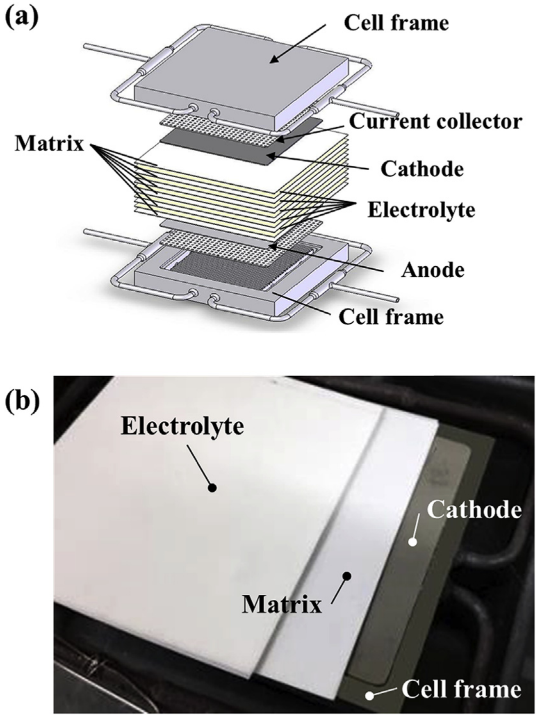


Fig. 1 – MCFC single cell: (a) schematic of MCFC single cell, (b) cathode cell frame and components of MCFC single cell.

Table 1 – MCFC single-cell operating conditions and components.

Temperature		620 °C
Pressure		1 atm
Sealing pressure		0.2 MPa
Gas utilization		0.4 at 150 mA/cm^2
Gas composition	Anode	$H_2/CO_2/H_2O = 72:18:10$
	Cathode	$Air/CO_2 = 70:30$

matrix of the cell, the degree of electrolytes impregnation into cell components, and the wet-seal construction are controlled [20]. The effects of the vibration were therefore considered and studied at sealing pressures of 0.2 MPa (normal operating condition) and 0.1 MPa in the MCFC operations.

Electrochemical impedance spectroscopy (EIS) was measured at open circuit voltage (OCV) to investigate the effects of vibrations on the charge transfer and mass transfer resistance of MCFCs. The parameters for EIS measurement were as follows: the frequency range set from 10^4 to 10^{-2} Hz with 10 point per decade and 5 mV of AC amplitude. To examine the cell durability at resonance frequencies, the resonance frequency of the cell was determined in the ranges from 1 to 50 Hz ($\Delta f = 1$ Hz) at 620 °C using hydraulic vibration system (MTS Landmark).

Vibration condition simulating marine environments

Two hydraulic pressure sets were used to simulate the vibration conditions of marine environments is shown in Fig. 2. The sealing pressure was applied to the cell frame using a hydraulic vibration system inside a heated chamber, and another external hydraulic vibration system (MTS Landmark) [21] was employed to induce vibrations with desired frequencies on the heat chamber enclosing the MCFC cell.

The mechanical effects of marine environments are mainly due to waves and winds. The vibration in marine environments can be categorized into wind waves and the swells [22]. Wind waves are surface waves by wind blowing over an ocean surface. Vibration generated by wind waves has a period in the range of 6–14 s. A swell is a series of mechanical waves propagating along the interface between the air and ocean. Vibration generated by swell has a period longer than 15 s. The amplitude and frequency of the artificial vibration were controlled in order to simulate marine environments.

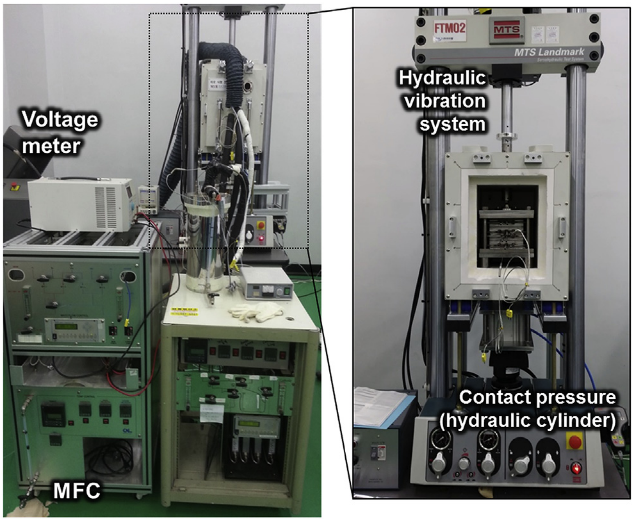


Fig. 2 – Experimental setup for simulating marine environments.

The vibration conditions for the marine environment are presented in Table 2. Four vibration conditions were chosen in order to simulate the vibration induced by sea winds and swell. In vibration condition A, the period of the vibration was 23–20 s (frequency of 0.043–0.05 Hz). The period of the vibration condition B was 19–17 s (frequency of 0.053–0.058 Hz). Vibration conditions A and B represent the vibration caused by swell. In vibration conditions C and D, which represent the vibration caused by wind waves, the frequency ranges were 0.071–0.083 Hz and 0.1–0.125 Hz, respectively.

Experimental results

Experimental results for MCFC single cell operating with 0.2 MPa sealing pressure

The performance of the MCFC single cell in marine environments was firstly evaluated with a sealing pressure of 0.2 MPa. The initial voltage of the single cell was 0.744 V at a current density of 150 mA/cm^2. After 130 h of operation for stabilization, the performance of the single cell was investigated with three different vibration conditions (Fig. 3).

The cell was firstly operated under vibration condition A for 130 h after which the cell voltage was 0.740 V at 150 mA/cm^2. No obvious voltage drop was observed after the operation under vibration condition A. Further vibration condition B and C was consequently applied to the cell for 108 and 126 h, respectively, and the cell voltage did not actually changed through the operations. Briefly, no reduction in the cell performance was observed under the sealing pressure of 0.2 MPa.

To investigate the resistance component of the MCFCs, electrochemical impedance spectroscopy (EIS) analysis was conducted (Fig. 4). Nyquist plots obtained from the EIS analysis of the MCFCs have an intercept on the real axis indicating an ohmic resistance (R_0). The EIS results are also indicated by two semi-circles at high- and low-frequency ranges, representing the resistance related to electrochemical reactions, or charge-transfer resistance (R_{ct}) and mass-transfer resistance (R_{mt}), respectively.

Fig. 4 shows the EIS results obtained from the cell at a sealing pressure of 0.2 MPa after 0, 45, and 120 h of operations under the vibration condition C. However, EIS analysis did not

Table 2 – Conditions used to simulate the vibration effects exerted on marine MCFC.

Vibration condition	Period (s)	Frequency (Hz)	Source
A	20–23	0.043–0.05	Swell
B	17–19	0.053–0.058	
C	12–14	0.071–0.083	Wind wave
D	8–10	0.1–0.125	

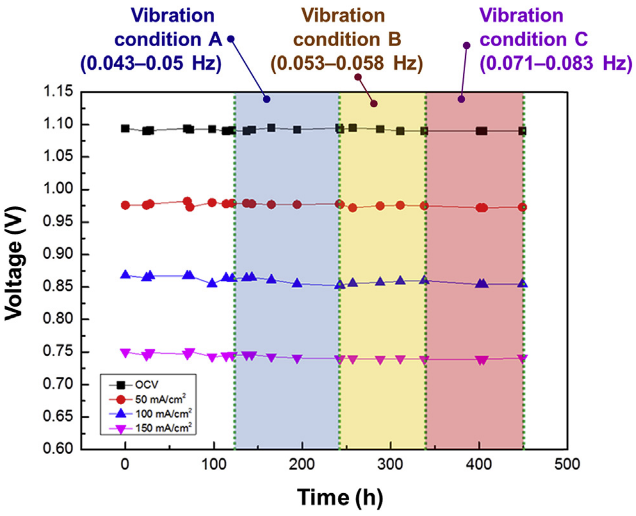


Fig. 3 – MCFC single-cell performance in marine-environment vibration system, operating at 0.2 MPa sealing pressure.

exhibit a significant difference of the cell resistances through the measurements. It can be inferred that the vibration environment does not affect the performance of the MCFC single cells in vibration condition C under the normal operating conditions (0.2 MPa sealing pressure).

Experimental results for MCFC single cell operating at 0.1 MPa sealing pressure

Next, the cell was operated at a sealing pressure of 0.1 MPa, which is half the value of the normal operating condition. As shown in Fig.5, after operation of the cell at 0.1 MPa for 455 h, the open-circuit voltage was 1.081 V. The voltage of the cell at the current density of 150 mA/cm^2 was 0.794 V. Then, the cell was operated for 269 h in vibration condition A, which represents swelling vibration environments. The voltage of the cell at the current density of 150 mA/cm^2 decreased to 0.77 V.

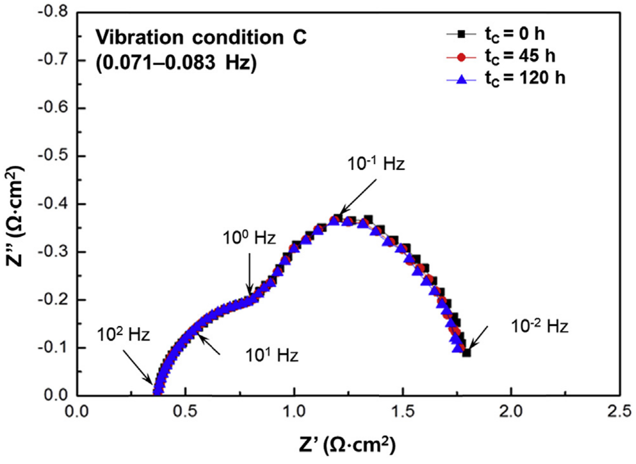


Fig. 4 – EIS results with respect to operating time in vibration condition C at sealing pressure of 0.2 MPa.

Subsequently, the vibration was stopped for 224 h. The voltage of the cell at the current density of 150 mA/cm^2 increased to 0.776 V. Vibration condition C was again applied to the cell for 169 h. The voltage of the cell at the current density of 150 mA/cm^2 decreased to 0.761 V. After stopping vibration condition C for 239 h, the voltage of the cell at the current density of 150 mA/cm^2 increased by 7 mV, to 0.768 V. Finally, vibration condition D was applied to the cell for 288 h. The voltage of the cell at the current density of 150 mA/cm^2 decreased to 0.74 V.

At the sealing pressure of 0.1 MPa, after applying vibration to the MCFC single cell, its performance decreased. When the vibration was stopped, the voltage of the cell increased slightly. Compared with the 0.2 MPa sealing pressure case, the performance of the cell was influenced by the vibration.

The values of the voltage drop at 150 mA/cm^2 of current density under vibration conditions A, C, and D were 24, 15, and 28 mV, respectively (see Fig. 5). Moreover, the voltage drop was greater when the current density was higher. Typically, the mass-transfer resistance is the main polarization in the high-current-density region. The cell voltage drop in the high-current-density region had a greater effect attributed to the increased mass-transfer resistance caused by the vibration. EIS analysis also confirmed that R_{mt} was increased as the vibration continues (Fig. 6). However, R_0 and R_{ct} did not change with or without the vibration of the cell. The results indicate that vibration induced by the wind waves and swelling increased mass transfer resistances, but not the ohmic resistance or the charge-transfer resistance.

During the operation at the sealing pressure of 0.2 MPa, the performance of the single cell was not changed by the vibration of the marine environment, as shown in Fig. 3. In contrast, at the sealing pressure of 0.1 MPa, the performance of the cell decreased because of the vibration. Thus, it is apparent that the vibration of marine environments reduces the performance of the MCFC single cell at low sealing

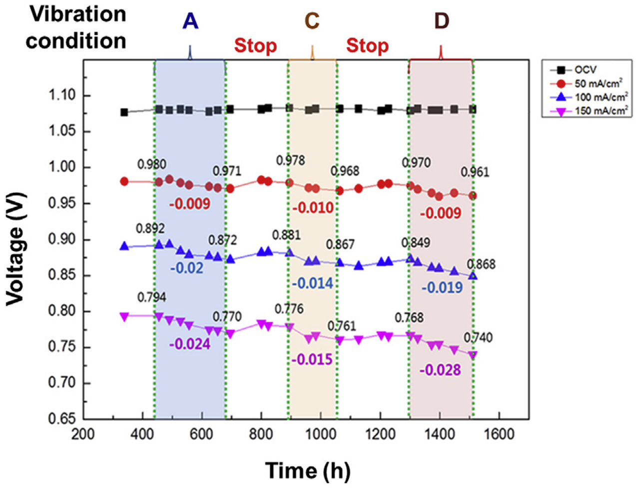


Fig. 5 – MCFC single-cell performance in marine-environment vibration system, operating at 0.1 MPa sealing pressure.

pressure. The voltage drop due to the vibration is a major obstacle for stable operation in marine environments. For long-term and stable operation of MCFCs in marine environments, the performance degradation due to the mass-transfer resistance should be minimized.

Discussion

EIS characterization of MCFC single cell in vibration environments

The increase in mass transfer resistance due to the gas diffusion limit would induce an electrolyte loss, leading to the increasing of ohmic resistance and the electrode polarization [18]. Experimental results reported by Morita et al. [18] indicated that the voltage-decay rate under normal operation is 3.3 mV/1000 h.

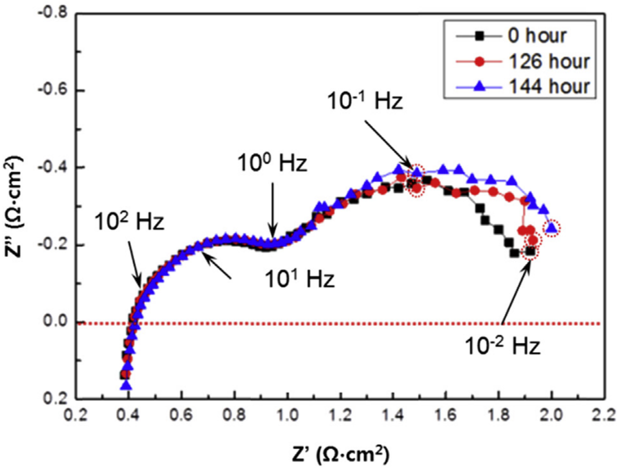
The voltage decay rate in the vibration environment shown in Fig. 5 is significantly large compared to the normal operation case (at the sealing pressure of 0.2 MPa). From these results of MCFC single cell operations under various conditions, it was expected that the increase in the mass transfer resistance in the vibration condition at a sealing pressure of 0.1 MPa occurs on the cathode side. In order to investigate the increase in the mass-transfer resistance due to marine vibration, the composition of the cathode gas was changed for MCFC single cell operation at the sealing pressure of 0.1 MPa. The cathode gas for MCFC operation is typically composed of 70% air and 30% CO_2 where air comprises 78% N_2, 21% O_2, and small amounts of Ar, CO_2, etc.

To study the effects of mass transfer in the presence of vibrations on MCFC, two different cathode gases were used in EIS measurements; air (70%)/CO_2 (30%) mixture and pure O_2 (41.2%)/CO_2 (58.8%) gases. Before the EIS analysis, the cell was operated at 150 mA/cm^2 for 120 h in vibration condition D (0.1–0.125 Hz), which exhibited the largest performance degradation. The EIS results for the two cases are shown in Fig. 7(a) and (b), respectively. When air and CO_2 are used as the cathode input gas, R_{mt} became larger after vibration condition D was applied to the MCFC single cell. In contrast, when oxygen was used instead of air, the vibration had no effect on the performance of the single cell, as shown in Fig. 7(b).

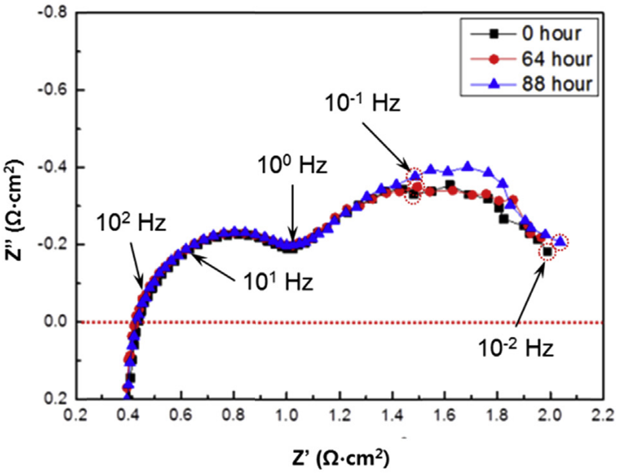
The increased R_{mt} in the EIS results indicates that the O_2 in the cathode gas is difficult to transfer to the triple-phase boundary of the electrode. In marine environments, diffusion of the N_2 and O_2 might occur competitively owing to the vibration and low sealing pressure.

In order to maintain the initial performance of the cell, the proper sealing pressure should be applied to the cell to minimize the mass-transfer resistance. Using O_2 and CO_2 gas as the cathode input gas instead of air and CO_2 would also resolve the performance reduction due to vibration environments.

(a) Vibration condition A
(0.043–0.05 Hz)



(b) Vibration condition C
(0.071–0.083 Hz)



(c) Vibration condition D
(0.1–0.125 Hz)

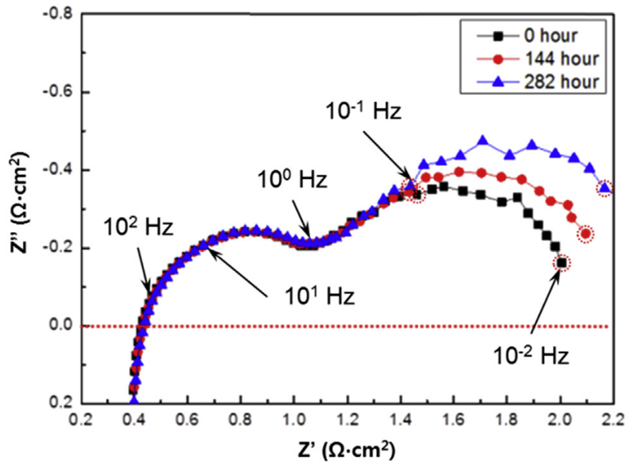
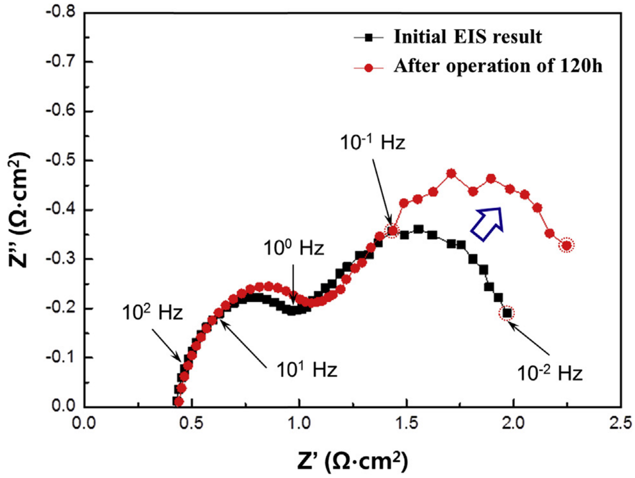


Fig. 6 – MCFC single cell EIS results with respect to operating time in vibration conditions A, C, and D: (a) vibration condition A, (b) vibration condition C, (c) vibration condition D.

(a) Cathode input gas – Air (O_2+N_2) + CO_2



(b) Cathode input gas – O_2 + CO_2

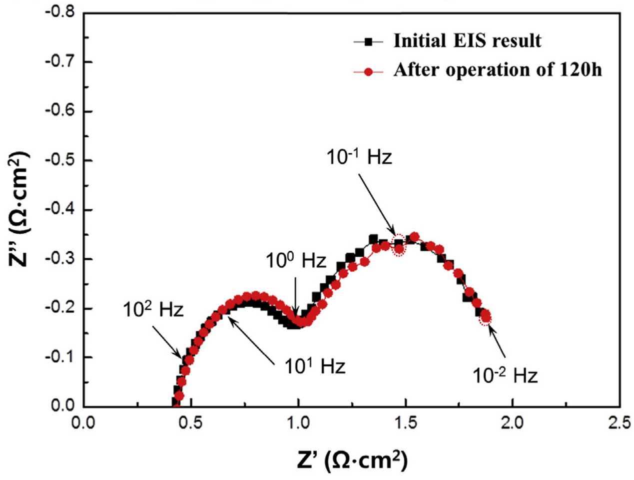


Fig. 7 – Variation in mass-transfer resistance according to marine-environment vibration at 0.1 MPa sealing pressure: (a) Cathode input gas – Air + CO_2, (b) Cathode input gas – O_2 + CO_2.

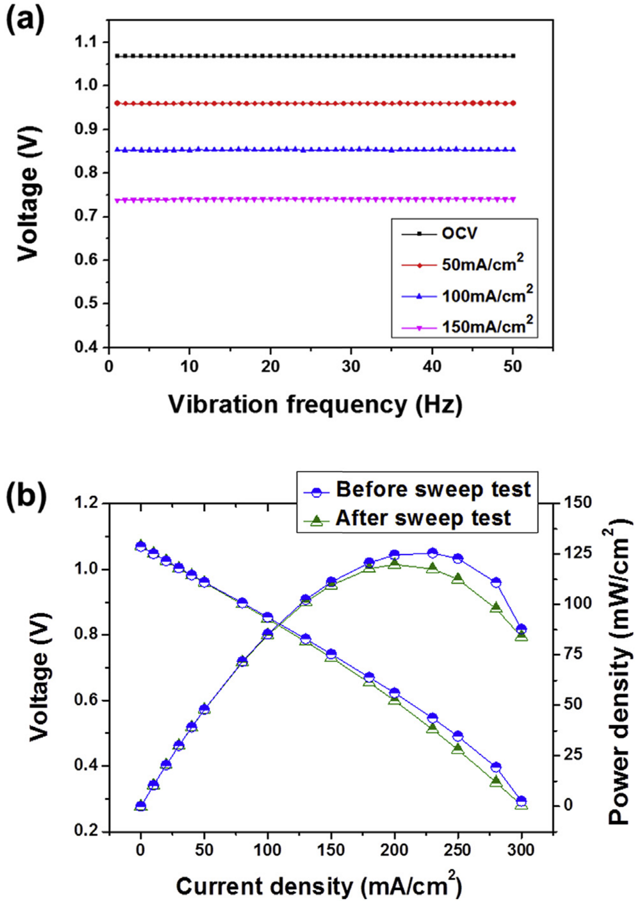


Fig. 8 – Performance of MCFC single cell in the sweep test: (a) Voltage distribution with respect to vibration frequency, (b) I–V and power-density curves after 90 min of durability test.

MCFC single-cell performance under vibration frequency sweep

For the APU, the vibration due to marine environments and ships occurs in a wide frequency range. The effect of various oscillation frequencies from 1 to 50 Hz was therefore investigated on the MCFC cell performance (Fig. 8). These vibration conditions (frequency of 1–50 Hz) can be induced by a ship's motion and diesel engines. With sealing pressure of 0.2 MPa, the minimum and maximum cell voltage was 0.738 and 0.742 V at the current density of 150 mA/cm^2 with the vibration frequencies swept. The cell was stably operated with insignificant voltage changes, approximately 3 mV in the vibration frequencies studied.

Although the MCFC performance was stable at various vibration frequencies scanned, the cell vibration at certain frequencies can be a major problem for stable operation as the system oscillated with greater amplitude at the resonance frequency [23]. The mechanical resonance of cells can cause fracture and breakage of internal components such as the anode, cathode, matrix with the electrolyte, and wet-seal, potentially yielding gas cross-over, which induces critical damage to the cell.

The resonance frequency of the MCFC single cell was determined using hydraulic vibration system. The vibration amplitude was maximized at the resonance frequency of 13 and 29 Hz. The tubes connected with cell the frames extremely trembled at 13 Hz of resonance frequency. In contrast, only cell reacted to the vibration at 29 Hz of resonance frequency. Therefore, 29 Hz of frequency was assumed the resonance frequency of the cell.

Then, the cell durability was studied at the current density of 150 mA/cm^2 and sealing pressure of 0.2 MPa in the vibration condition of 29 Hz for 90 min Fig. 8b shows the I–V and power-density curves for the MCFC single cell after 90 min of the durability test. However, the voltage of the cell was marginally decreased by 35 mV at 250 mA/cm^2. The results again indicated that the resonance vibration frequency

(29 Hz) had no significant effect on the performance of the MCFC single cell in relatively short operation time of 90 min [24]. For a more accurate analysis of the actual operation in the marine environments, it is required to conduct long-term studies of MCFCs under additional vibration conditions. Moreover, the investigation of the complex phenomenon combining the vibration environment and the marine atmosphere is needed.

Conclusion

A molten-carbonate fuel cell (MCFC) single cell was operated in vibration environments to investigate the applicability of MCFCs as auxiliary power units (APUs) in marine environments. To simulate the marine environment, a vibration system was constructed with two hydraulic cylinders.

The sealing pressure was varied to investigate its effect on the performance of the MCFC single cell. The vibration conditions were classified into four modes according to the wind wave and swell. At a sealing pressure of 0.2 MPa, the vibration did not affect the cell performance. However, at a sealing pressure of 0.1 MPa, the performance decreased under all vibration conditions. An EIS test indicated that the mass-transfer resistance increased at the sealing pressure of 0.1 MPa, but this did not occur when oxygen was used as the cathode gas instead of air. The resonance frequencies of cell vibration were determined as 13 and 29 Hz. When the sealing pressure was 0.2 MPa, the resonance did not affect the performance of the cell. In summary, proper sealing pressures should be applied to the cell for stable operations in marine environments. O_2 and CO_2 gas are recommended as the cathode input gas rather than air and CO_2 to mitigate the increased mass-transfer resistance induced by the cell vibration.

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