Short communication

Effects of marine atmosphere on the cell performance in molten carbonate fuel cells

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HIGHLIGHTS

► Cell performance is increased with increasing impregnated NaCl amount in cathode.
► Accumulated Na^+ ion gives positive effect on cell performance.
► HCl doesn't cause severe corrosion because emitted HCl level is below 1 ppm.

ARTICLE INFO

ABSTRACT

The effects of NaCl, a main component in seawater, on molten carbonate fuel cell (MCFC) performance is investigated using a single cell test with 1, 5, and 10 wt.% NaCl-impregnated cathodes for marine applications. The cell performance increases with increasing amounts of impregnated NaCl in the cathode. This cell performance enhancement is due to the reduction in the charge transfer resistance of the electrode. From the analysis of the electrolyte composition using the inductively coupled plasma (ICP) and ion chromatography (IC) methods after cell operation, it is confirmed that the Na^+ ions are accumulated in the carbonate melts, and approximately 80 at.% of the Cl- ions are emitted into the anode outlet as HCl. Expecting that the emitted HCl causes severe corrosion of the utilities, the concentrations of accumulated Na^+ ions of emitted HCl in the anode outlet are calculated when air with a sea-salt particle concentration of 5–500 ugm^{-3} is supplied to the MCFC stack. Although HCl is a very corrosive gas, it is expected that the emitted HCl does not cause severe corrosion because, even at a high sea-salt concentration of 500 ugm^{-3}, the emitted HCl concentration is low enough to operate the stack safely.

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1. Introduction

Marine transport accounts for only 3% of global petroleum consumption but contributes 14% of the NO_x and 16% of the SO_x global emissions due to diesel being used as fuel [1]. Currently, the marine industry is under pressure to reduce emissions and become more environmentally friendly. Thus, the marine industry has focused on the use of fuel cells (FCs) as auxiliary power units (APUs) because fuel cells can provide several advantages over diesel, such as low emission levels, high efficiency, and silent and vibration-free electricity generation [2,3]. Fuel cells convert the chemical energy of a gaseous or gasified fuel directly into electricity via electrochemical reactions and, therefore, unlike conventional thermal engines, are not limited by Carnot efficiency.

It is known that the typical required power of a fuel cell stack ranges from 250 kW up to several MWs for marine applications [1]. Among the currently available fuel cell technologies, molten carbonate fuel cells (MCFCs) and polymer electrolyte membrane fuel cells (PEMFCs) are considered the most promising candidates for marine applications. Additionally, solid oxide fuel cells (SOFCs) have, in theory, the highest potential but are currently not sufficiently developed for applications. Although the MCFC start-up process takes longer than that for PEMFCs [4], the marine application of MCFCs is actively studied in many countries because MCFCs operate at a high temperature with a high tolerance to air-contamination and carbon monoxide, a contaminant found in fuel [5].

For marine applications of MCFCs as APUs, the inflow of new impurities into the MCFC stack has to be considered because, in a marine atmosphere, seawater mists can be introduced into the cathode side via air, which is one of the reactant gases [6]. Table 1 shows the general seawater composition [7]. As shown in Table 1,

Table 1
Composition of generic seawater [7].

Elements	Composition (%)
Cl	1.937
Na	1.077
SO_4	0.271
Mg	0.130
Ca	0.041
K	0.039
CO_3	0.002
Br	0.007
Total	3.504

Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, and CO_3^{2-} are major components of seawater. Of the above-mentioned components, it is expected that Mg^{2+}, Ca^{2+}, K^+, and CO_3^{2-} produce no negative effects on the cell performance of MCFC stacks. Because K^+ and CO_3^{2-} ions are the main components of a MCFC electrolyte, these components are dissolved in the carbonate melts if they enter the MCFC stacks. It is expected that Mg^{2+} and Ca^{2+} have positive effects on the cell performance of MCFC stacks. Mg^{2+} is added to the cathode intentionally to reduce Ni dissolution in the carbonate melts because this dissolution causes short-circuiting during long-term operation [8]. According to Frangini and Scaccia [9], the addition of small amounts of Ca^{2+} to carbonate melts enhances the O_2 solubility of the melts and improves the oxygen reduction reaction (ORR), which is an electrochemical reaction on the cathode side that enhances cell performance. By contrast, the SO_4^{2-} impurity in seawater produces a negative effect on the cell performance. According to the report by Watanabe et al. on exposing MCFC stacks to impurities [10], exposure of only 1 ppm SO_2 decreased the cell performance of a 1 kW stack, largely due to the sulfur poisoning effect.

Although several articles expected that a NaCl impurity would produce a negative effect on an MCFC stack [1,5,11–13], there are no reports that experimentally show the effects of a NaCl impurity on the cell performance of MCFCs. As shown in Table 1, NaCl is a main component of seawater. Thus, the study of this NaCl effect is important for marine applications. In this study, the NaCl effect on the cell performance of MCFCs is examined. Because NaCl exists as a solid due to its high melting point (800 °C), it is difficult to continuously introduce NaCl into the cathode side using air. Therefore, a NaCl-impregnated cathode was prepared, and its electrochemical performance was examined using a single cell test. Although it is difficult to simulate the real conditions of a marine atmosphere exactly, it is thought that the single cell test using a NaCl-impregnated cathode can give basic information on the NaCl effect on cell performance. From the experimental results of this test, the NaCl effect during MCFC stack operation in a marine atmosphere is inferred.

2. Experiment

To examine the NaCl effect on cell performance, 1, 5, and 10 wt.% NaCl-impregnated cathodes were fabricated by dip-coating a porous Ni plate into an NaCl aqueous solution. The amount of impregnated NaCl is controlled by varying the concentration of the NaCl aqueous solution. The NaCl-impregnated Ni plate was dried in an oven at 80 °C for 1 h.

The electrode performances of the NaCl-impregnated cathodes and a pure cathode were evaluated using a single cell with an active electrode area of 100 cm². Except for the cathodes, the conventional components, such as the Ni–Al anode, Li/K carbonate electrolyte, and Al fiber reinforced $LiAlO_2$ matrix, were identical for the single cell experiments. The single cells were operated at 620 °C. The gas compositions in the cathode and anode were Air:CO_2 = 7:3 and

H_2:H_2O:CO_2 = 72:18:10, respectively. A DC current was applied to the single cells using an electric loader (ELTO DC Electronics Co., ESL300Z). The single cells were operated at a current density of 150 mAcm⁻². To analyze the electrode polarization, electrochemical impedance analysis (EIS) was conducted using a Solartron S1287 and 1260A.

To investigate the impregnated NaCl states after cell operation, the elemental compositions of the electrolytes contained inside the matrices were examined using inductively coupled plasma (ICP) analysis. To confirm the Cl emission during cell operation, the anode outlet gas was soaked in distilled water for 5 h after introducing the reactant gas, and the existence of Cl^- was confirmed using the ion chromatography (IC) method.

To determine whether the NiO cathode reacts with NaCl, 0.2, 1, and 5 wt.% NaCl-impregnated Ni plates were heat-treated at 650 °C for 100 h in a box furnace, washed 3 times with distilled water, and then dried at 80 °C for 1 h. The crystal structures of the heat-treated samples were investigated by X-ray diffraction (XRD) using a D/Max2400 Rigaku diffractometer with Cu-Kα radiation.

3. Results and discussion

Before the electrochemical performance of the NaCl-impregnated cathode was tested, it was determined whether the NiO cathode reacts with NaCl. 0.2, 1, and 5 wt.% NaCl-impregnated Ni plates were heat treated in air at 650 °C for 100 h. After removing NaCl by washing the plates, XRD analysis was conducted, and the results are presented in Fig. 1. As shown in Fig. 1, the Ni plate is transformed into NiO due to heat treatment in an air atmosphere. In the MCFC, the porous Ni plates transform into a lithiated NiO cathode via lithiation and the oxidation process. If NaCl is doped into NiO, a peak shift phenomenon in the XRD pattern is observed due to the difference in radii between Ni and Na or between O and Cl. However, as shown in the narrow range of Fig. 1(b), a peak shift is not observed. This result indicates that the NiO cathode does not react with NaCl under these experimental conditions. It is expected that introducing NaCl through air does not damage the cathode material in an MCFC stack in a marine atmosphere.

To investigate the NaCl effect on the cell performance, the single cells using 1, 5, and 10 wt.% NaCl-impregnated cathodes and a pure cathode were tested. The single cells were operated at 620 °C. The cell voltages of the single cells using 0, 1, 5, and 10 wt.% NaCl-impregnated cathodes at a current density of 150 mAcm⁻² after 200 h of operation are presented in Fig. 2. As shown in this figure, the cell voltages increased with increasing amounts of impregnated NaCl. Although we expected the cell voltages to decrease with increasing NaCl amount due to NaCl poisoning of the electrode, the experimental results are not in accord with our expectations.

To understand the cell voltage changes as a function of NaCl-impregnated amount in the cathode, EIS analysis was conducted on single cells using 0, 1, 5, and 10 wt.% NaCl-impregnated cathodes, and these results are presented in Fig. 3. As shown in Fig. 3, the spectra obtained from the EIS analysis of MCFCs have intercepts on the real axis, indicating an ohmic resistance (R_o), and, generally, the spectra contain both high- and low-frequency semicircles. It is known that the high frequency semicircles represent the resistances related to the electrochemical reaction and that the low frequency semicircles represent the resistances related to mass transfer [14]. The charge transfer resistance (R_{ct}) in the high frequency semicircle and the mass transfer resistance (R_{mt}) in the low frequency semicircle can be extracted from the EIS data using an equivalent circuit [15]. The obtained resistances from the single cells using 0, 1, 5, and 10 wt.% NaCl-impregnated cathodes are summarized in Table 2. As shown in Table 2, there are no large