Deterioration in the Cathode Performance during Operation of the Microbial Fuel Cells and the Restoration of the Performance by the Immersion Treatment

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Abstract

Microbial fuel cells were operated with synthetic wastewater containing phosphate as a buffer and sodium acetate as a substrate. Linear sweep voltammetry showed the deterioration in the performance of the cathodes after operation (18-31% decrease of current density at 0.1V vs. Ag/AgCl). The immersion of the deteriorated cathodes in Milli-Q water and acidic and basic buffer solution improved the performance. The treatment with the acidic buffer solution restored the performance of the cathode to the extent almost equivalent to that of the cathode before operation (98-107% of current density at 0.1V vs. Ag/AgCl), whereas the treatment with Milli-Q water and the basic buffer solution did not restore the performance to that extent (92% of current density at 0.1V vs. Ag/AgCl). The improved performance by the immersion in Milli-Q water or the acidic buffer solution indicates that the water-soluble components are responsible for the deterioration in the cathode performance. Almost complete recovery of the performance in acidic condition suggests that salts that are highly soluble in acidic condition and poorly soluble in basic condition are responsible for the deterioration. The analysis of the eluted substances in the immersion solution suggests that these salts contained phosphorus, magnesium and calcium in a high concentration.

Keywords: Microbial fuel cell; Cathode performance; Immersion treatment; Deposition of alkaline salts

Introduction

A microbial fuel cell (MFC) uses the metabolism of electrogenic bacteria to convert the chemical energy stored in the organic substances in wastewater to the electrical energy [1-3].

There are a variety of MFC, today. The single-chamber MFC with an air-cathode had great advantages in terms of the structure (simpler), power density (higher), and aeration (not required) [4,5], and therefore, it has been considered the most anticipated model for practical application. The generation of electricity in these single-chamber MFCs, however, has been reported to decline during the course of continuous operation [6,7]. Previous studies [6-9] indicated that the deterioration in the performance of the cathode was one of the possible causes [6-9]. Saito et al. [8] assumed that the formation of biofilm over the cathode is a possible cause of the performance deterioration. They washed away the biofilm formed over the cathodes of their MFC reactors after eight months (128 cycles) of operation using deionized water. The result showed the increase of maximum power density in all the reactors, compared with that before removing biofilm, but it did not restore the performance to the extent equivalent to that of the initial stage of operation. Kiely et al. [6] removed the biofilm of the cathode that had been operated for one year by washing away with deionized water, and found the increase of maximum power density as in the case of Saito et al. [8], but could not restore the performance of the cathode to the extent equivalent to that of a new cathode. These results suggested that the cathode biofilm is only one of the main reasons for cathode performance deterioration.

Jiang et al. [9] reported that gradual fouling of calcium and sodium in wastewater over the cathode surface was responsible for the increased internal resistance of the MFCs, thereby reducing the generation of electricity. When the fouling substance was removed by a paper towel, the internal resistance of the MFCs dropped from 150 Ω to 120 Ω, and the power density increased from 600 mW/m² to 1200 mW/m² in the 6th week of the operation. However, when the same procedure was implemented in the 9th week, although the internal resistance dropped from 260 Ω to 200 Ω, the power density did not increase, remaining at 300 mW/m². Jiang et al. [9] suggested the possibility that the longer operation time led to stronger adhesion of the fouling substance on the cathode surface, which could not be removed by simple wiping [9].

Zhuang et al. [7] argued that the formation of alkali salts inside the cathode covered the catalytic surface, thereby preventing contact between oxygen and the surface of catalyst. They rinsed the cathode of the MFC that had been operated for 60 days using deionized water until the pH of the rinsed water became neutral, and determined the cathode performance before and after rinsing using linear sweep voltammetry (LSV). The LSV results confirmed that the rinsing restored the performance of the cathode to the extent close to that of the 20th day of operation.

As described above, although the biofilm has long been thought to be responsible for the deterioration of the cathode performance, it has been found that there were some other causes as well. Some adhering substances on the cathode were also thought to be responsible, but the removal of the substances could not restore the performance of the cathode to the extent close to that of the initial stage of operation in the previous studies. It is suspected that the incomplete restoration of the performance might be due to the incomplete removal of the adhering substances.

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It was reported previously that the treatment of the wastewater containing phosphorus (P), magnesium (Mg) and ammonium (NH₄) by MFCs led to the deposition of struvite crystal on the cathode [10]. Furthermore, the treatment of the wastewater containing P, Mg, but not NH₄ led to the deposition of cattiite, a type of magnesium phosphate. The deposition could be explained by the following mechanism: the pH increase in the vicinity of the cathode due to the oxygen reduction reaction, decreased the solubility of struvite and cattiite, leading to the deposition of these compounds. The LSV detected the deterioration in the performance of the cathode where struvite deposited even though no biofilm existed, but the removal of struvite by the immersion treatment in Milli-Q water (pH 7.0) and 2-morpholinoethanesulfonate (MES) buffer solution (pH 5.5) restored the performance of the cathode to the extent equivalent to that of a new cathode. The pH increase of the MES buffer solution from 5.5 to 6.3 suggested that the elution of alkaline salts had occurred. Also, the cathode performance of the control group (without biofilm) deteriorated, although the extent of deterioration was not as large as the one where struvite deposited. The immersion treatments of both groups in Milli-Q water (pH 7.0), and the MES buffer solution (pH 5.5) restored the performance of the cathodes to the extent equivalent to that of a new cathode. These results suggested the possibility that the deposition of the (alkaline) salt over the surface or inside of the cathode, whose solubility was decreased due to increased pH in the vicinity of the cathode, prevented mass transfer between the solution and the cathode, thereby deteriorating the performance. Hence, removing the deposition should restore the performance of the cathode. We thought that the salt would deposit in the basic condition, and therefore we would be able to remove the salt effectively by immersing the deteriorated cathode in the acidic solution.

In this research, we examined how the conditions of the immersion treatment influenced the restoration of the deteriorated cathodes, by running the air-cathode single-chamber MFCs and immersing the deteriorated cathodes in the acidic buffer solutions having a variety of pH. We used the LSV to evaluate the cathode performance.

Materials and Methods

Preparation of the air-cathodes

Carbon paper (Toray Carbon Paper TGP-H-120, Toray Industries, Inc., Japan) was used as a base of the air-cathodes. According to the method described by Cheng and Liu [11], coating of platinum catalyst (TEC 10ES50E, the amount of platinum 2.5 mg/cm², Nafion binder) was applied to the inner surface of the reactor, and PTFE was applied to the outer surface of the reactor so that it would work as an air diffusion layer. The projected area of the air cathode was set to 47 cm² (7.7 cm diameter).

Structure of the reactor and operation for acclimatization

Six identical air-cathode single-chamber MFCs were operated. Figure 1 shows a schematic diagram of the MFC reactor. The effective capacity of the reactor was 70 ml. The anode was made of carbon felt with a diameter of 7.7 cm (projected area 47 cm²) and a thickness of 1 cm (LFP-210, Osaka Gas Chemicals Co., Ltd., Japan), fixed by a graphite rod with its one end connected to the external circuit. A piece of polyethylene nonwoven fabric (2×3.5 cm, 0.5 cm thick) was placed over the cathode to prevent direct contact with the anode. The MFC reactor was then connected to a 300 ml glass bottle filled with a synthetic wastewater, and the internal solution was circulated at a flow speed of 20 ml/min, according to the method described by Borole et al. [12]. The bottle was replaced by a new bottle filled with the synthetic wastewater containing the materials other than the substrate every five to ten days. The external resistance was set to 10 Ω.

The reactor was provided with the synthetic wastewater, containing sodium acetate as a substrate, a 100 mM phosphate buffer solution (NaH₂PO₄·36 mM, Na₂HPO₄·64 mM, NH₄Cl·12 mM, KCl·3.5 mM, pH 6.8, electrical conductivity 11.2 mS/cm), minerals and vitamins described in previous publication [10]. The reactor was operated at room temperature. Sodium acetate was continuously added at the rate of 8.1 mmol/L-day with a syringe pump as a substrate, and the synthetic wastewater containing the above components was replaced by exchanging the bottle every five to ten days. A piece of anode with biofilm was taken off with the tweezers from a previously operated MFC, and placed next to a new anode as inoculum.

The acclimatization operation was performed for more than 50 days, and the generation of approximately 4 A/m² electric current was observed in all the MFC reactors.

The immersion treatment of the cathodes and installation to the reactors

Six new identical air-cathodes (C1-C6) were prepared, and three of them were treated by immersing in acidic buffer solutions. The C1, C2 and C3 cathodes were immersed in 300 ml of a 30 mM citrate buffer solution (pH 3.0), 300 ml of a 30 mM acetate buffer solution (pH 4.5), and 300 ml of a 30 mM MES buffer solution, respectively, for 24 hours, then rinsed with Milli-Q water, and finally dried in the oven at 40°C overnight (Immersion Treatment 0). The C4-C6 cathodes were not immersion-treated. The old cathodes of the reactors which had completed the acclimatization operation were replaced with the above C1-C6 cathodes, and then the reactors were operated for 50 days. The immersion pretreatments for the C1, C2 and C3 cathodes had two purposes: (1) if the performance of the cathode after operation was improved by the immersion treatment, to determine whether such observed improvement was in fact due to the restoration of the performance that had deteriorated during operation or the improvement that could happen even before operation; (2) to determine if the immersion pretreatment had any effects on the extent of deterioration of the cathode performance during operation as well as the restoration of the performance by the immersion treatment after operation.

Restoring the performance of the cathodes

The cathodes after operation were rinsed in Milli-Q water to
remove the biofilm formed over the surface, and dried in the oven at 40°C. Thereafter, the C1 and C4 cathodes were immersed in 500 mL of a 30 mM citrate buffer solution (pH 3.0) for 24 hours. Likewise, 24-hour immersion was performed for the C2 cathode in 500 mL of a 30 mM acetate buffer solution (pH 4.5), the C3 and C5 cathodes in 500 mL of a 30 mM MES buffer solution (pH 5.5), and the C6 cathode in 500 mL Milli-Q water. All of them were then rinsed in Milli-Q water, and dried in the oven at 40°C overnight (Immersion Treatment 1). Further 24-hour immersion (Immersion Treatment 2) was done for the C1 and C2 cathodes in 500 mL of a 30 mM MES buffer solution (pH 5.5), and the C6 cathode in 500 mL of a 30 mM CHES buffer solution (pH 9.2). All of them were then rinsed in Milli-Q water, and dried in the oven at 40°C. Table 1 summarizes the treatments done for all the cathodes.

We thought that the deposition of the salts whose solubility was lower in the basic condition was responsible for the deterioration of the cathode performance, so we conducted the immersion treatments in the acidic condition, where such salts were more soluble. The immersion treatment in Milli-Q water was conducted, to eliminate the possibility of water-soluble salts. The immersion treatment in the basic condition was conducted just for comparison.

**Evaluation of the cathode performance**

The performance of the cathodes was evaluated by the LSV. MFCs having the same structure as the one used for operation were provided (C1-C6), immediately after operation of the MFCs (C1-C6), after Immersion Treatment 1 (C1-C3), and after Immersion Treatment 2 (C1-C2, C6). The pH of the solution where the immersion treatments were performed was measured, and the elemental analysis of the same cathode when compared with the untreated ones. The MES-treated (pH 5.5) cathode and citrate-treated (pH 3.0) cathode at the electric potential of 0.2 V or below, but no substantial difference was observed in the acetate-treated (pH 4.5) cathode when compared with the untreated ones. The MES-treated (pH 5.5) cathode and the citrate-treated (pH 3.0) cathode exhibited similar tendencies, which were different from the one of the acetate-treated (pH 4.5) cathode. This result indicates that the effect does not have simple pH dependence.

**Deterioration in the cathode performance during operation**

Figure 4 shows the change of the current density over time during operation of the MFCs. Six MFCs exhibited almost identical behavior in the fluctuation of the current density during operation of the MFCs, that is, the current density dropped to approximately 2.5 A/m² immediately after the replacement of the cathodes, then gradually increased, and reached about 4 A/m² around the 15th day, and became stable without any noticeable decline of the amount of power generation until the end of operation (data not shown).

**Results and Discussion**

**Change of the performance of the unused cathodes by Immersion Treatment 0**

Figure 2 shows the linear sweep voltammogram of new cathodes when they were prepared. Because the electric potential of the cathodes in previously operated MFCs of the same structure was about 0.1 V vs. Ag/AgCl (data not shown), the current density of the cathodes was evaluated primarily over the range of 0-0.2V. When the performance of the new cathodes before Immersion Treatment 0 was evaluated, the OCP fell within the range from 0.54 V to 0.60 V (vs. Ag/AgCl), and the current densities were within the range from -4.5 to -5.7A/m² at 0.2 V (vs. Ag/AgCl), from -7.5 to -9.6A/m² at 0.1 V (vs. Ag/AgCl), from -12.3 to -14.4A/m² at 0 V (vs. Ag/AgCl). The OCP of the cathodes that had undergone the immersion treatment dropped by approximately 0.1 V, regardless of the type of the buffer solution used (Figure 3). The current increased in the MES-treated (pH 5.5) cathode and citrate-treated (pH 3.0) cathode at the electric potential of 0.2 V or below, but no substantial difference was observed in the acetate-treated (pH 4.5) cathode. The MES-treated (pH 5.5) cathode and the citrate-treated (pH 3.0) cathode exhibited similar tendencies, which were different from the one of the acetate-treated (pH 4.5) cathode. This result indicates that the effect does not have simple pH dependence.
In summary, the immersion of the cathode in Milli-Q water after operation was further immersed in the MES buffer solution (pH 5.5), which contributed toward restoring the performance of the cathode. The extent of recovery of the cathode performance by the immersion treatment with the basic buffer solution: When C6 (untreated before operation) was immersed in Milli-Q water after operation was further immersed in the CHES solution (pH 9), the current density decreased over the range from the OCP to 0.05 V (vs. Ag/AgCl) but increased elsewhere (Figure 6-f). As compared with the density at the end of operation, the current density decreased over the range from the OCP to 0.2 V (vs. Ag/AgCl) (Figure 6-f). The current density at 0.1 V (vs. Ag/AgCl) after the immersion treatment in Milli-Q water was 92% of the density before operation, which declined to 89% of the density before operation after the immersion treatment in the CHES solution (pH 9). These results suggest that the immersion treatment in the basic buffer solution does not contribute to the restoration of the cathode performance as much as the acidic buffer solution does.

The relationship between the pH of the buffer solutions and the effect of improvement of the cathode performance: Compared with the restoring effect of the cathodes exhibited by the immersion treatment by the pH 4.5 acetate was small (C2: 8.8 A/m² at 0.1V vs. Ag/AgCl) (Figure 8). These results suggest that the improvement of the cathode performance by the immersion treatment has no simple dependence on the pH; it is not such that the lower pH the greater the recovery, it has an optimum value of pH, or it is greater below certain value of pH; rather, it has a more complicated mechanism.

The difference of the effect of the acetate buffer solution and the MES buffer solution: When the cathode (C2), which had been immersed in the acetate buffer solution after operation was further immersed in the MES buffer solution, the performance of the cathode was improved to the extent almost equivalent to that of C1, C3, C4, and C5, which had undergone the immersion treatment (10.0 A/m² at 0.1V vs. Ag/AgCl) (Figure 6-b). This result suggests that the components which had not been removed by the immersion in the acetate buffer solution were removed by the immersion in the MES buffer solution, which contributed toward restoring the performance of the cathode.

When C6 (untreated before operation) was immersed in Milli-Q water after operation was further immersed in the CHES solution (pH 9.2), the current density decreased over the range from the OCP to 0.05 V (vs. Ag/AgCl), but increased elsewhere. Furthermore, after the CHES immersion treatment, the current density decreased over the range from the OCP to 0.2 V (vs. Ag/AgCl), as compared with the density at the end of operation (Figure 7f).
are responsible for the deterioration in the cathode performance. Furthermore, the immersion of the cathode in the acidic solution contributed more to the restoration of the cathode performance than did the immersion in water. This result suggests that some acid-soluble components (such as alkaline salts) are responsible for the deterioration in the performance. These ideas agree with the hypothesis that the localized increase of pH in the vicinity of the cathode contributes to the deposition of the alkaline salts on the cathode.
Eluted components in the solution

Figure 9 shows the concentration of P, Mg, Mn, Co, and Ca²⁺ in the solution where the immersion treatment of the cathodes was performed.

P, Mg, Mn, and Co was detected in a higher concentration in the solutions, where the immersion treatments of the cathodes were performed after operation (Immersion Treatment 1) than in the solutions where the immersion treatments were performed before operation (Immersion Treatment 0). Among these elements, Mg, Mn, and Co was detected in a higher concentration in the acidic solutions than in Milli-Q water (pH 7.0) or the basic solution (pH 9.2). These results suggest that Mg, Mn and Co accumulated as alkaline salts during operation, and the removal of these salts by elution due to
**Figure 8:** Comparison of the performance of the cathodes after the immersion treatment 1. (C1: cathode 1 treated in citrate buffer (pH 3.0) → citrate buffer (pH 3.0), C2: cathode 2 treated in acetate buffer (pH 4.0) → acetate buffer (pH 4.0), C3: cathode 3 treated in MES buffer (pH 5.5) → MES buffer (pH 5.5), C4: cathode 4 not treated → citrate buffer (pH 3.0), C5: cathode 5 not treated → MES buffer (pH 5.5), C6: cathode 5 not treated Milli-Q water (pH 7.0)).

**Figure 9:** The amount of P, Mg, Mn, Co, and Ca\textsuperscript{2+} eluted from the cathodes in the immersion treatments.
the immersion treatments restored the performance of the cathode. The dissolving concentration of P remained almost constant, having no dependence on pH of the solutions. Therefore, P might have deposited as a water-soluble salt that was soluble under pH 9.2. Though the concentration of Ca\(^{2+}\) ion could not be quantified in the acetate buffer solution because of the higher background concentration in measurement, Ca\(^{2+}\) ion was detected in a higher concentration in the acidic solutions than in Milli-Q water or the basic solution. This result suggests that Ca also accumulated over the cathode as an alkaline salt like Mg, Mn, and Co.

In the previous research, the authors reported that when the wastewater containing P, Mg, and NH\(_4\) was treated in the MFC, struvite crystal deposited on the cathode, and when the wastewater containing P and Mg but not NH\(_4\) was treated, cattiite crystal deposited on the cathode [10]. The greater elution of P and Mg than any other inorganic mineral elements from the cathode in this research suggests that the compound containing P and Mg indeed deposited on the cathode. However, the molar ratio of Mg to P became 3.4-4.5 in the acidic solutions, which was higher than the molar ratio of struvite to P (1) or cattiite to P (1.5). The higher molar ratio of Mg suggests that the magnesium salts containing no phosphorus, such as magnesium carbonate and magnesium hydroxide, accounted for most of the magnesium deposition. In the meantime, Ca has been reported to be a main component of the deposition on the cathode to our knowledge to date [9,13,14], and found in a form of calcium carbonate [9,15]. In this research, because a great amount of Ca\(^{2+}\) also eluted into the solution, and a great amount of carbonate ion were assumed to be present in the internal solution of the MFCs as a result of decomposition of acetate, Ca is suspected to have accumulated in a form of calcium carbonate as reported in the literature.

The C1 and C2 cathodes underwent the immersion treatment twice after operation (Immersion Treatment 1, Immersion Treatment 2). Most of the elution of P, Mg, Mn, Co, and Ca\(^{2+}\) occurred in Immersion Treatment 1, and only a small amount of the elution occurred in Immersion Treatment 2. The performance of C2 was improved more after Immersion Treatment 2 than after Immersion Treatment 1. Therefore, the deterioration of the cathode performance may not be caused only by the accumulation of P, Mg, Mn, Co, and Ca\(^{2+}\).

Furthermore, in the solution where Immersion Treatment 1 was performed under acidic environment with three different pH (pH 3.0, 4.5, 5.5), no substantial difference was observed in the eluted amounts of P, Mg, Mn, Co, and Ca\(^{2+}\). However, when treated with the pH 3.0 and pH 5.5 solutions, the performance of the cathode was restored to the extent almost equivalent to that of a new cathode, but it was not restored to such extent when treated with the pH 4.5 solution. This result suggests that there can be yet another cause or causes for the deterioration in the performance of the cathode, in addition to the accumulation of P, Mg, Mn, Co, and Ca\(^{2+}\).

Conclusion

When the MFCs were operated with the synthetic wastewater containing a 100 mM phosphate buffer solution, the decline of the power output was detected in all the six reactors due to the deterioration in the cathode performance. When the cathodes were removed and immersed in the buffer solutions with a variety of pH, the performance was improved in all of them. The extent of improvement was greater in the immersion treatment in the acidic buffer solution than in the neutral or basic buffer solution; particularly, in the immersion treatment in the citrate (pH 3.0) and MES (pH 5.5) buffer solutions, the performance was restored to the extent almost equivalent to that of an unused cathode. Almost complete restoration of the cathode performance by the immersion under the acidic environment suggests that the components responsible for the deterioration are salts which are highly soluble in the acidic environment and poorly soluble in the basic environment.

In practical application of MFCs, one of the challenges is the deterioration of the cathode performance, which leads to the increase of the running cost. In this research, some of the properties of causative agents of cathode deterioration were identified and one of the preventive measures was presented.

Real wastewater contains a wider variety of substances than synthetic wastewater; therefore, the effect of the deposition on the cathode as well as the extent of recovery by elution would be different from the results presented. Hence, further research based on the real wastewater is needed.

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