

Cathodic Reduction of Cu<sup>2+</sup> and Electric Power Generation Using a Microbial Fuel CellZejie Wang,<sup>†</sup> Bongsu Lim,<sup>†</sup> Hui Lu,<sup>†</sup> Juan Fan,<sup>†</sup> and Chansoo Choi<sup>\*</sup>

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When Cu<sup>2+</sup> was used as an electron acceptor, removal of Cu<sup>2+</sup> was achieved from the synthesized wastewater (SW) in the cathode compartment of a microbial fuel cell (MFC). By addition of KNO<sub>3</sub>, the different initial pH of the SW showed no effect on the removal efficiency of Cu<sup>2+</sup>. For Cu<sup>2+</sup> concentration of 50 mg/L the removal efficiencies were found to be 99.82%, 99.95%, 99.58%, and 99.97% for the KNO<sub>3</sub> concentrations of 0, 50, 100 and 200 mM, and to be 99.4%, 99.9%, 99.7%, and 99.7% for pH values of 2, 3, 4, and 5, respectively. More than 99% Cu<sup>2+</sup> was removed for the Cu<sup>2+</sup> concentrations of 10, 50, and 100 mg/L, while only 60.1% of Cu<sup>2+</sup> was removed for the initial concentration of 200 mg/L (pH 3). The maximum power density was affected by both KNO<sub>3</sub> concentration and initial concentration of Cu<sup>2+</sup>. It was increased by a factor of 1.5 (from 96.2 to 143.6 mW/m<sup>2</sup>) when the KNO<sub>3</sub> concentration was increased from 0 to 200 mM (50 mg/L Cu<sup>2+</sup>), and by a factor of 2.7 (from 118 to 319 mW/m<sup>2</sup>) when Cu<sup>2+</sup> concentration was increased from 10 to 200 mg/L (pH 3).

**Key Words:** Copper ion removal, Electron acceptor, Electric power generation, Microbial fuel cell

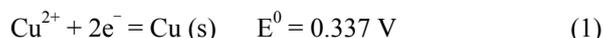
## Introduction

Heavy metals from contaminated water are of major concern because of their high toxicity and susceptible carcinogenic effect to many life forms. Unlike organic contaminants, which are mostly biodegradable, metal ions do not degrade into harmless end products. Cu<sup>2+</sup> may be present in wastewaters from a variety of sources that use copper salts or copper catalysts. Some sources include chemical manufacturing processes and plating baths. Thus the effective removal of copper from polluted waters is ecologically very important. Many technologies were reported for the removal or recovery of copper from wastewater including bio-sorption,<sup>1</sup> activated carbon adsorption,<sup>2</sup> chemical precipitation,<sup>3</sup> acidification,<sup>4</sup> and adsorption on minerals.<sup>5,6</sup> Majority of the technologies mentioned above have their inherent limitations, such as high costs and harmful effluents. Therefore, it is very important to develop new technologies to remove copper ions from wastewater efficiently and economically.

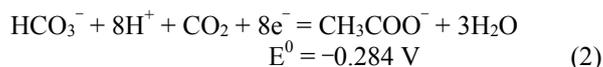
MFCs raise more attention due to the benefits of both wastewater treatment and power generation.<sup>7,8</sup> In a dual-compartment MFC, anode and cathode compartments are separated by an ion exchange membrane, such as proton exchange membrane (PEM),<sup>9</sup> cation exchange membrane (CEM), anion exchange membrane (AEM), and ultrafiltration membrane,<sup>10</sup> and bipolar membrane.<sup>11</sup> In the anode compartment microorganisms attach to the anode surface, and degrade organic pollutants under anaerobic conditions to generate electrons. The generated electrons flow through an external circuit to the cathode, reacting with electron acceptors and producing an electric current. Several variations of wastewater have been used as electron donors, including artificial wastewater,<sup>12</sup> brewery wastewater,<sup>13</sup> vegetable products,<sup>14</sup> landfill leachate,<sup>15</sup> chemical wastewater,<sup>16</sup> etc. Even if the majority of wastewaters were used as electron donors in the anode compartment until now, only a few studies were focused on the treatment of wastewater used as electron accep-

tors. Li *et al.*<sup>17</sup> tried treatment of electroplating wastewater containing Cr<sup>6+</sup> by using MFC. They got Cr<sup>6+</sup> removal efficiency as high as 99.5% and maximum power density of 1600 mW/m<sup>2</sup>. Clauwaert *et al.*<sup>18</sup> removed up to 0.146 kgNO<sub>3</sub><sup>-</sup>/m<sup>3</sup> day for the net cathode compartment volume, and the highest power output was 8 W/m<sup>3</sup> for the net cathode compartment volume by using a bio-cathode of the MFC.

The reduction potential of Cu<sup>2+</sup>/Cu is as follows:



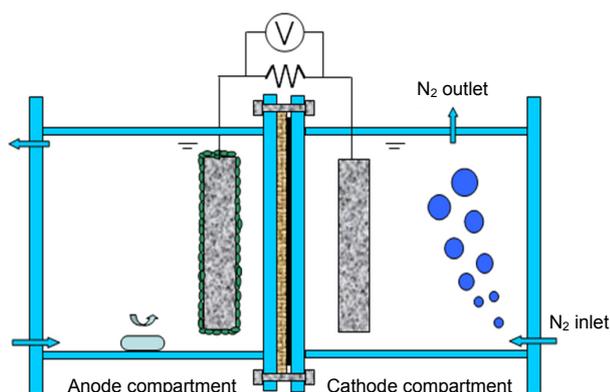
The reduction potential of HCO<sub>3</sub><sup>-</sup>/CH<sub>3</sub>COO<sup>-</sup> at pH 7 is as follows:



From Eq. (1) and (2), the cell voltage ( $E_{\text{cmf}}$ ) of a MFC using acetate as electron donor and Cu<sup>2+</sup> as electron acceptor can be calculated:

$$E_{\text{cmf}} = E^0_{\text{ca}} - E^0_{\text{an}} = 0.337 \text{ V} - (-0.284 \text{ V}) = 0.621 \text{ V}$$

Therefore, the  $E_{\text{cmf}}$  is theoretically enough to remove Cu<sup>2+</sup> and to generate electric power as well. Our goal of this study is to remove Cu<sup>2+</sup> contaminants from the wastewater, while generating power at the same time, and to evaluate factors that could affect the removal of Cu<sup>2+</sup> and power generation. To avoid the transfer of Cu<sup>2+</sup> from the cathode chamber to the anode chamber, which would be toxic to microorganism, AEM was selected as a separator of the reactor chambers instead of usually used PEM, such as Nafion membrane. This study is the first time to combine the removal of Cu<sup>2+</sup> contaminants and power generation by using a MFC.



**Figure 1.** Schematic of the MFC used to remove  $\text{Cu}^{2+}$  and to generate electric power.

### Experimental Section

**MFC fabrication.** A tubular dual-compartment MFC reactor fabricated with a plexi-glass tube (diameter = 5 cm) was used in this study (Figure 1). Both anode and cathode compartments held a volume of 137 mL (length = 7 cm), and the effective volumes were 120 mL and 100 mL, respectively. The anode and cathode compartments were separated by AEM (AMI-7001, Membrane International, Inc., USA) with a surface area of  $19.6 \text{ cm}^2$  (diameter = 5 cm). The AEM was preconditioned by immersing in NaCl solution as described in the published paper.<sup>10</sup> Both anode and cathode were graphite felts with the same geometrical surface area of  $35.6 \text{ cm}^2$  (length = 3.5 cm, width = 3 cm, height = 1.12 cm, Alfa Aesar, USA). The electrodes were treated by soaking in acetone overnight; afterwards the electrodes were rinsed with distilled water 5 times, and then heated for 30 min at  $450 \text{ }^\circ\text{C}$  in a muffle furnace as reported by Wang *et al.*<sup>19</sup>

**Inoculation.** Anaerobic sludge, collected from the anaerobic digester of Okchen wastewater treatment plant in Okchen, Korea, was used as inoculum in the anode compartment. To start up the MFC reactor, a mixture of 30 mL anaerobic sludge and 90 mL artificial wastewater (AW) was pumped into the anode compartment after purging with nitrogen gas for 5 min. The AW contained 1.36 g/L  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ , 1.05 g/L  $\text{NH}_4\text{Cl}$ , 1.5 g/L  $\text{KH}_2\text{PO}_4$ , 2.2 g/L  $\text{K}_2\text{HPO}_4$ , and 0.2 g/L yeast extract.<sup>20</sup> Each time the voltage decreased below 25 mV, 0.2 g medium was added to the anode compartment until a repeatable maximum voltage was obtained. The cathode compartment was filled with 0.1 M  $\text{KH}_2\text{PO}_4$  solution and purged with air (80 mL/min) during the inoculation stage. The external circuit was connected with a 500 ohm resistor. Titanium wire was used to collect current. Experiments were performed at  $30 \text{ }^\circ\text{C}$  in a temperature-controlled incubator (C-IN, Changshin Scientific CO., Korea).

**Operational conditions.** After the MFC was successfully started, the solution in the anode compartment was replaced with fresh AW purged with  $\text{N}_2$  for 5 min to remove dissolved oxygen. A buffer solution of our batch-fed MFC was used as the anolyte, and its running time was 11 hours, as scheduled. After the scheduled running time the anolyte was replaced with a fresh anolyte to keep the pH constant at 7. To balance the charge, the anions,

such as phosphate ions, can also be transported through the AEM from the cathode chamber, and can neutralize the protons. So, there were no adverse effects on microbial activity due to the proton accumulation during the experiments. In order to remove them by the accumulation of protons in the anode chamber, the pH would be better controlled by using a continuously fed MFC with the pH adjustment. A magnetic stirring bar was used to constantly stir the anolyte in the anode compartment. The cathode compartment was also refilled with SW, which was prepared by dissolving  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  in distilled water. To eliminate the effect of dissolved oxygen, the cathode compartment was continuously purged with  $\text{N}_2$  (80 mL/min). The effect of ionic conductivity of catholyte solution in the cathode compartment on power generation was evaluated by adding different amounts of  $\text{KNO}_3$  to the SW. In order to determine the removal efficiency of  $\text{Cu}^{2+}$  under different pH values, the pH of SW was adjusted with diluted  $\text{HNO}_3$ .

**Calculations.** Voltage was measured with a potentiostat (WMPG 1000, Won-A Tech, Korea) every minute. The power density was calculated according to:

$$P = \frac{V^2}{RA}$$

where V is the voltage, R is the external resistance, and A is the geometrical surface area of the anode.

The coulombic efficiency (CE) was calculated as follows:

$$CE = \frac{8 \int_0^t Idt}{Fv\Delta\text{COD}}$$

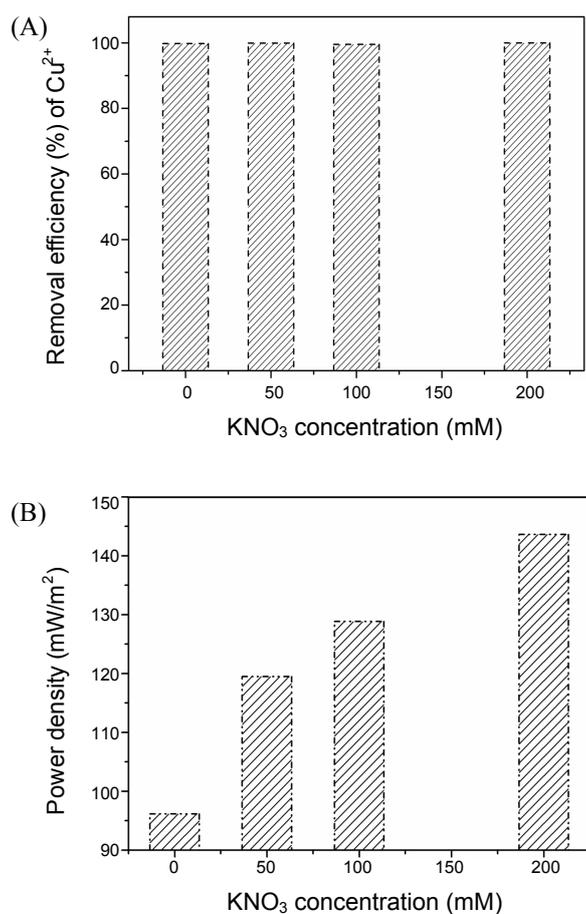
where 8 is a constant used for COD, based on  $M_{\text{O}_2} = 32$  for the molecular weight of  $\text{O}_2$  and 4 for the number of electrons exchanged per mol of oxygen, t is the reaction time interval (60 s), F is the Faraday's constant ( $96485 \text{ C/mol e}^-$ ), v is the effective volume of anode chamber, and  $\Delta\text{COD}$  is change of the chemical oxygen demand consumed, I is current calculated as:

$$I = \frac{V}{R}$$

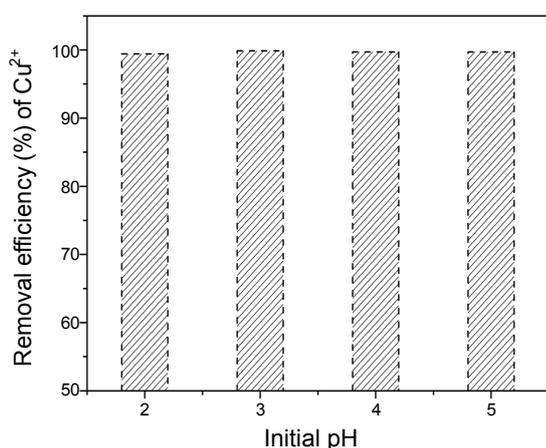
**Analysis.** The concentration of total copper was analyzed with an ICP emission spectrometer (ICPE-9000, Shimadzu, Japan). Observation of removal product attached on the surface of the cathode was performed with SEM (XL-30S FEG, Phillips, Holland). The chemical elements of the deposit on the cathode surface after reaction was identified with EDS (Quantax 200, Bruker, Germany).

### Results and Discussion

**Effects of  $\text{KNO}_3$  concentration.**  $\text{KNO}_3$  was not necessary for the reduction of  $\text{Cu}^{2+}$ . As shown in Figure 2A, the removal efficiency of  $\text{Cu}^{2+}$  was not affected by the addition of  $\text{KNO}_3$



**Figure 2.** Effect of  $\text{KNO}_3$  concentration on (A)  $\text{Cu}^{2+}$  removal and (B) power generation.



**Figure 3.**  $\text{Cu}^{2+}$  removal efficiencies under different pH values.

within a reaction time of 11 hours, which was at least 99.6%, while the maximum power output was greatly improved (Figure 2B). The maximum power density was increased from 96.2 to 143.6  $\text{mW}/\text{m}^2$ , when  $\text{KNO}_3$  concentration was increased from 0 mM to 200 mM. The reason for this is that the addition of  $\text{KNO}_3$  could decrease the internal resistance of the MFC by improving the ionic conductivity of the solution. Similar phenomenon was reported by Liu *et al.*,<sup>21</sup> when KCl was used to im-

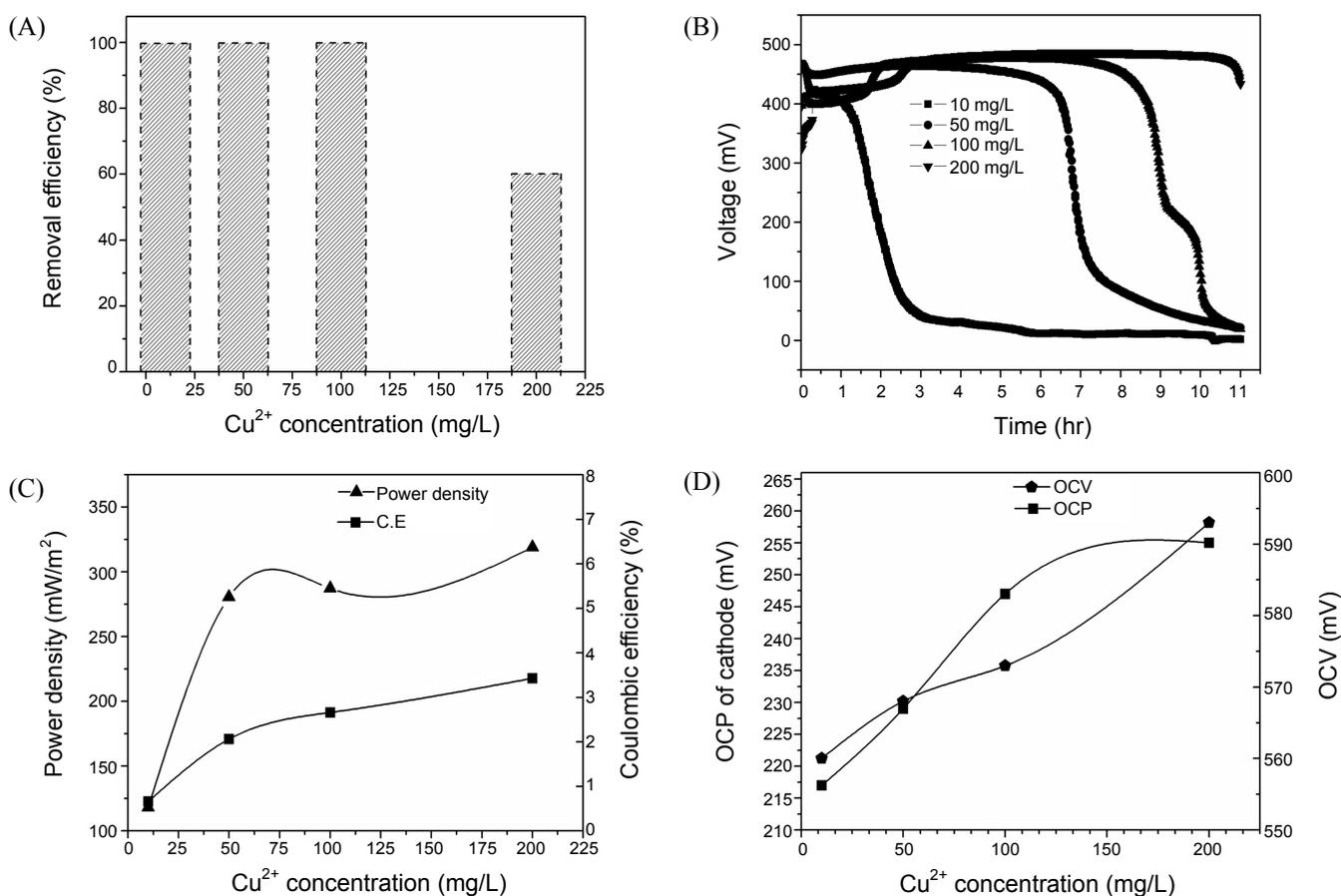
prove the ionic conductivity. In this study, the internal resistance was decreased from 239.4 to 136.1 ohm due to the improved ionic conductivity by increasing  $\text{KNO}_3$  concentration from 0 to 200 mM (pH 5.8, unadjusted). According to electron stoichiometry calculation, the coulombs used to generate electric current were increased from 18.45 C to 18.97 C according to the increase in  $\text{KNO}_3$  concentration from 0 to 200 mM, and they were a little larger (1.5% to 4.4%) than those used to reduce  $\text{Cu}^{2+}$ . The loss of electrons was likely due to the reduction of dissolved oxygen in SW during the early stage of  $\text{N}_2$  purge.

**Effects of initial pH.** To determine the effects of pH on the removal efficiency of  $\text{Cu}^{2+}$ , SW was prepared by dissolving 50 mg/L  $\text{Cu}^{2+}$  in 200 mM  $\text{KNO}_3$  solution. The pH was adjusted from 2 to 5. After operating the cell for 11 hours, the removal efficiencies were found to be 99.4%, 99.9%, 99.7%, and 99.7% for pH values of 2, 3, 4, and 5, respectively. From the result, it can be concluded that the  $\text{Cu}^{2+}$  removal was obviously not affected by the initial pH of the SW. The conclusion was consistent with the principle that the reduction of  $\text{Cu}^{2+}$  did not involve protons according to Eq. (1), which meant that no adjustment of pH was needed for treatment of practical wastewater containing  $\text{Cu}^{2+}$  by using MFC. This is different from other reported technologies<sup>5,6</sup> indicating that higher pH led to higher removal efficiency of  $\text{Cu}^{2+}$ . Although the existence of  $\text{H}^+$  in SW had no effect on the reduction of  $\text{Cu}^{2+}$ , the adjustment of pH also affected the power generation due to the decrease of internal resistance by increasing ionic conductivity (data not shown). This also differed from other kinds of electron acceptors, such as  $\text{Cr}^{6+}$ <sup>17</sup> and  $\text{MnO}_4^-$ <sup>22</sup> showing that reduction is largely affected by  $\text{H}^+$  concentration.

**Effects of initial  $\text{Cu}^{2+}$  concentration.** Effects of initial concentration of  $\text{Cu}^{2+}$  on the removal efficiency and power generation were also evaluated by adjusting the concentration of  $\text{Cu}^{2+}$  to 10, 50, 100, and 200 mg/L (200 mM  $\text{KNO}_3$ , pH 3). Figure 4A shows that, within 11 hours, the removal efficiencies of  $\text{Cu}^{2+}$  reached 99.72%, 99.86%, and 99.92% for the  $\text{Cu}^{2+}$  concentrations of 10, 50, and 100 mg/L, respectively, while only 60.1% of  $\text{Cu}^{2+}$  was reduced for the concentration of 200 mg/L. This was probably due to the fact that the electrons produced by the microorganisms in the anode compartment was insufficient for the reduction of  $\text{Cu}^{2+}$  compared to its high concentration and limited operation time as shown in Figure 4B.

The open circuit potential (OCP) of the cathode was determined by placing an Ag/AgCl (3.3 M KCl) reference electrode in the cathode compartment. Then it was converted with respect to Standard Hydrogen Electrode (SHE). Power density was greatly affected by the initial concentration of  $\text{Cu}^{2+}$  as shown in Figure 4C. The maximum power density increased by a factor of 2.7 from 118 to 319  $\text{mW}/\text{m}^2$ , when the initial concentration of  $\text{Cu}^{2+}$  was increased from 10 to 200 mg/L. The OCV increased from 563 to 590 mV for the same increase in the concentration of  $\text{Cu}^{2+}$  (Figure 4D). The improvement of maximum power density might be due to the increase in the OCP of the cathode which was influenced by  $\text{Cu}^{2+}$  concentration. This result was generally consistent with the trends expected by analysis using Nernst equation based on Eq. (1):

$$E = 0.337 + 0.030 \log [\text{Cu}^{2+}]$$



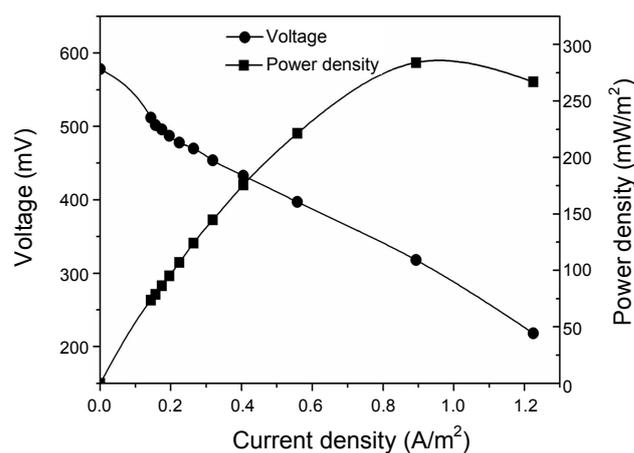
**Figure 4.** Effects of initial concentration of  $\text{Cu}^{2+}$  on (A) removal efficiency, (B) discharge voltage, (a) 10 mg/L, (b) 50 mg/L, (c) 100 mg/L, and (d) 200 mg/L, (C) power generation and coulombic efficiency, (D) open circuit potential of cathode and open circuit voltage.

A similar phenomenon was observed by You *et al.*,<sup>22</sup> when permanganate was used as an electron acceptor. Another reason for the improvement of the maximum power density would be the reduction of internal resistance caused by the increase in ionic conductivity with high initial  $\text{Cu}^{2+}$  concentration. The internal resistance was further reduced from 85.9 (10 mg/L  $\text{Cu}^{2+}$ ) to 63.7 ohm (200 mg/L  $\text{Cu}^{2+}$ ). The redox potential of  $\text{NAD}^+/\text{NADH}$  on the anode of our MFC was about  $-0.340$  V, which was close to that of  $-0.32$  V reported by other researchers.<sup>23</sup> The CE increased from 0.66% for 10 mg/L  $\text{Cu}^{2+}$  and from 3.43% for 200 mg/L  $\text{Cu}^{2+}$  (Figure 4C). This increase in CE was due to the increase of number of electron acceptors provided at higher  $\text{Cu}^{2+}$  concentrations, which led to relatively longer discharge time with higher voltage under the fixed load resistor (Figure 4B).

Figure 5 shows the power density curve as a function of current density for the  $\text{Cu}^{2+}$  concentration of 50 mg/L at pH 3. The external resistance was changed from 1000 to 50 Ohm. As it is illustrated, the maximum power density of  $284 \text{ mW}/\text{m}^2$  was achieved at a current density of  $0.893 \text{ A}/\text{m}^2$  with an external resistance of 100 ohm.

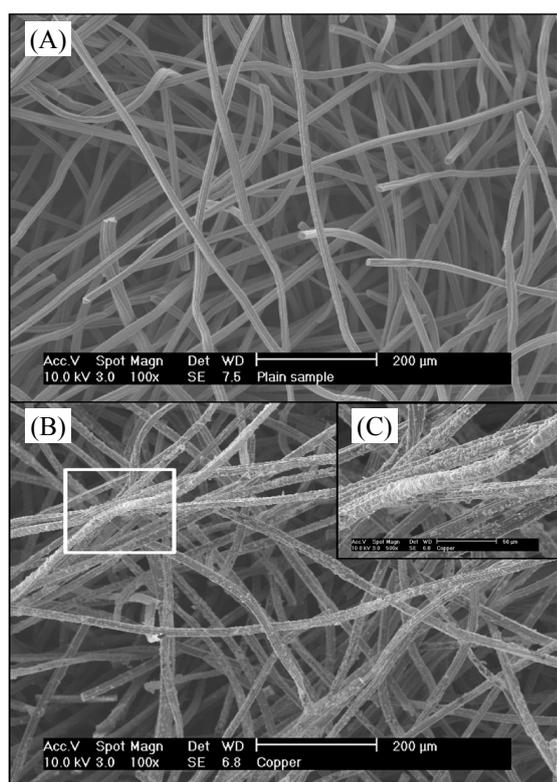
#### Characteristics of the cathode surface after MFC operation.

The cathode surface was observed using SEM and analyzed by EDS. As seen from the SEM picture (Figure 6), a deposit was clearly observed on the surface of the cathode after MFC



**Figure 5.** Power density curve as a function of current density (50 mg/L  $\text{Cu}^{2+}$ , pH 3).

operation in the  $\text{Cu}^{2+}$  solution. From the EDS analysis (Figure 7), the peaks at 0.943, and 8.096 keV verified that the copper metal exists on the surface of the cathode.<sup>24</sup> As discussed in the above,  $\text{Cu}^{2+}$  can be efficiently reduced and removed by accepting electrons generated by decomposition of acetate by microorganisms using a MFC. Compared to other technologies, the removal of  $\text{Cu}^{2+}$  using MFC has the following advantages: (1) It is not

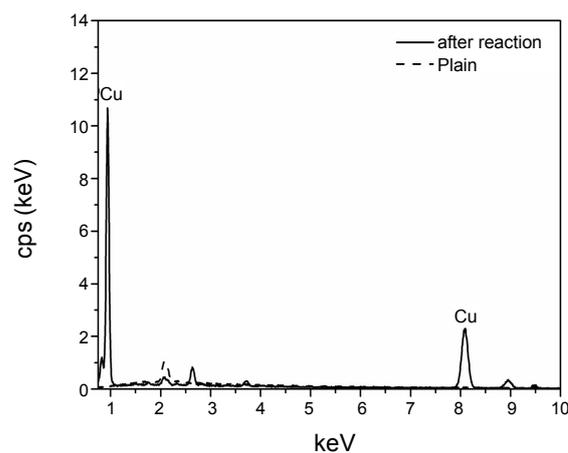


**Figure 6.** SEM pictures of (A) plain cathode, (B) cathode after the reaction, and (C) a magnification of the framed part in (B) (reaction time of 78 hr).

necessary to adjust the pH, while, as it was reported by Shukla and Roshan,<sup>5</sup> lower pH led to lower  $\text{Cu}^{2+}$  removal efficiency, thus costing extra to adjust the pH in order to get higher  $\text{Cu}^{2+}$  removal efficiency; (2) Electric power, a useful energy source, can be generated at the same time; (3) Pure copper can be easily recovered. From the EDS analysis and a color change of the cathode surface (from black to wine), the final product attached to the surface of the cathode was found to be copper metal. Actually, the graphite felt cathode would gradually turn to a copper cathode as the reduction of  $\text{Cu}^{2+}$  proceeded, which made it easy to recover the copper. Otherwise, a physical process, such as adsorption,<sup>1,6</sup> made it impossible to recover copper directly. In this study, the effective removal of  $\text{Cu}^{2+}$  from SW was achieved. However, further test of this technology should be performed using real wastewater containing  $\text{Cu}^{2+}$ . Its real application would depend on the development of a large scale-up of the MFC.

### Conclusions

This study successfully verified dual functions of  $\text{Cu}^{2+}$  removal from the synthesized wastewater and power generation of a dual-compartment microbial fuel cell. Addition of  $\text{KNO}_3$  and initial pH of SW showed no effect on the removal of  $\text{Cu}^{2+}$ , while the addition of  $\text{KNO}_3$  and adjustment of pH greatly affected the maximum power density due to the decrease of internal resistance. Initial concentration of  $\text{Cu}^{2+}$  affected both the re-



**Figure 7.** EDS analysis of the deposit on the surface of cathode (reaction time of 78 hr).

moval efficiency and the maximum power density. The maximum power density increased from 96.2 to 143.6  $\text{mW/m}^2$  when the  $\text{KNO}_3$  concentration was increased from 0 to 200 mM (50  $\text{mg/L Cu}^{2+}$ ), and from 118 to 319  $\text{mW/m}^2$  when the  $\text{Cu}^{2+}$  concentration was increased from 10 to 200  $\text{mg/L}$  (pH 3). The high removal efficiency of  $\text{Cu}^{2+}$  and high power generation achieved by our MFC makes the MFC a promising technology to treat  $\text{Cu}^{2+}$  contaminated water and recovery of copper metal.

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