



# Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology

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## ARTICLE INFO

### Article history:

Received 30 September 2011

Received in revised form

27 December 2011

Accepted 1 January 2012

Available online 9 January 2012

### Keywords:

Microbial fuel cells

Vanadium (V)

Chromium (VI)

Wastewater treatment

Electricity generation

## ABSTRACT

Vanadium (V) and chromium (VI) are the main metals found in vanadium containing wastewater with large amount and great toxicity. In present study, reduction of V(V) and Cr(VI) together with electricity generation is successfully achieved in double chamber microbial fuel cells (MFCs) by employing vanadium containing wastewater as the cathodic electron acceptor. The V(V) and Cr(VI) reduction efficiencies for 240 h operation approach up to  $67.9 \pm 3.1\%$  and  $75.4 \pm 1.9\%$ , respectively, with a maximum power density of  $970.2 \pm 20.6 \text{ mW m}^{-2}$ . The power output is enhanced, compared with the results from MFCs with V(V) as the sole electron acceptor, while the decrease of the cathode efficiency caused by deposits from Cr(VI) reduction process can also be mitigated. After reduction, chromium is mainly deposited on the cathode surface in the form of Cr(III), while most of vanadium can be precipitated from the exhausted catholyte by adjusting pH, thus treating vanadium containing wastewater successfully with energy harvest based on MFC technology. The operating principles of MFCs with two different electron acceptors are also reported for the first time.

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## 1. Introduction

Vanadium containing wastewater with low pH from vanadium mining and vanadium pentoxide manufacture is often produced in large quantities and can be greatly toxic [1]. Vanadium (V) and chromium (VI) are the main metals found in wastewater discharged after vanadium precipitation, with concentrations usually in the range from 100 to 400 mg L<sup>-1</sup> and pH of 2–4 [2]. Vanadium is harmful to people, and sometimes can be fatal. The toxicity of vanadium depends on its oxidation state, with V(V) being more toxic than other species [3]. Cr(VI), identified as one of 17 chemicals posing the greatest threat to human health, is a well-known mutagen, teratogen, and carcinogen besides being highly corrosive [4]. Previous methods for Cr(VI) removal from wastewater have included the use of cationic and anionic ion-exchange resins, chemical and electrochemical precipitation, membrane filtration and sorption [5], which may be operated with high cost. Moreover, these methods also generate large amount of sludge that is difficult to dispose and can hardly recover valuable metals from the treatment process [4]. Nowadays, few publications are presently available that address technologies for removal and recovery of V(V) from vanadium con-

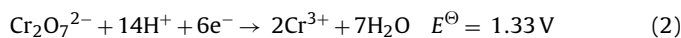
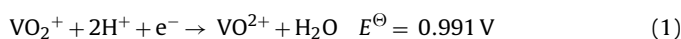
taining wastewater without sludge generation [6], especially when V(V) and Cr(VI) occur together.

Microbial fuel cells (MFCs) are devices that use bacteria as catalysts to oxidize organic or inorganic matter and generate electricity [7–9]. MFCs are capable of simultaneous biological electricity generation and wastewater treatment, and so offer an economic pathway to a sustainable energy future [10–12]. Electron acceptors in the cathode compartment play an important role in MFC performance. Oxygen and ferricyanide ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ) are most widely used for laboratory-based research on MFCs [13–15]. Recently, certain pollutants with high electrochemical redox potentials that are present in wastewater have been applied as electron acceptors in MFCs, while being reduced at the same time [16]. To the authors' knowledge, our research group was the first to report on the reduction and recovery of V(V) by means of MFC technology employing V(V) as the electron acceptor [2]. V(V) acted as the sole electron acceptor in our previous research, which is not the case in practice for vanadium containing wastewater discharged after vanadium precipitation. At the same time, little attention has been paid to the principle of the MFCs operated with multiple electron acceptors in MFC research field at present. This issue is worth investigating and the principles should be revealed as electron acceptors from wastewaters may be presented together in the actual circumstances.

In the present study, V(V) and Cr(VI) are considered together. Both have high electrochemical redox potentials (Eqs. (1) and (2))

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especially in vanadium containing wastewater with low pH, and act as electron acceptors in the MFCs, resulting in V(V) and Cr(VI) reduction simultaneously and electricity generation as follows.



The power output and the reduction efficiency of the metals are evaluated in present study. The principle of operating MFCs with two different electron acceptors and the behavior of the two metal ions after reduction is also investigated herein.

## 2. Materials and methods

### 2.1. Construction of the double chamber MFCs

Six double chamber MFCs were fabricated from cylinders, as described in our previous research [2]. The anode and cathode compartments were separated by a proton exchange membrane (Nafion117#, Dupont, USA). All of the anode and cathode electrodes were made of carbon fiber felt of dimensions 40 mm × 40 mm × 3 mm. The MFCs were connected to the data acquisition system (Measurement Inc., USA) by copper wires, and the voltage recorded at 5 min intervals. All of the anode compartments for the six MFCs were airproofed to prevent oxygen in the ambient air poisoning electrochemically active microbes in the anode compartment. The cathode compartments of the six MFCs were also sealed up to avoid oxygen acting as electron acceptor instead of V(V) or Cr(VI) in the cathode compartment.

### 2.2. Inoculation and electrolyte conditions

The six MFCs were inoculated with 25 mL sludge and effluent (containing adapted microbial consortium) from other well established MFCs operated for about half a year in the laboratory at Peking University. The microbes in the MFCs were first obtained from the anaerobic sludge of an up-flow anaerobic sludge blanket reactor for high strength sulfate containing wastewater treatment with high efficiency [2]. After the domestication, the inoculated sludge was removed from the MFCs to avoid the consumption of organic matter because of the anaerobic digestion. The anode solution contained the following components (per L): 0.81 g of  $\text{C}_6\text{H}_{12}\text{O}_6$ ; 4.97 g of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ; 2.75 g of  $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ ; 0.31 g of  $\text{NH}_4\text{Cl}$ ; 0.13 g of  $\text{KCl}$ ; 1.25 mL of vitamin solution; and 12.5 mL of trace mineral element solution [17]. The initial pH of the anolyte was about 7. The phosphate buffer solution was added to moderate the pH decrease in the anode compartment. The six MFCs were divided into three groups equally. The condition of the anode compartment for each group was identical, while the cathode compartment of each group was filled with 250 mL catholyte with pH 2, which was simulated vanadium containing wastewater with V(V) and Cr(VI) concentrations each of 250 mg L<sup>-1</sup> (MFCs-I), V(V) containing solution with V(V) concentration of 500 mg L<sup>-1</sup> (MFCs-II), Cr(VI) containing solution with Cr(VI) concentration of 500 mg L<sup>-1</sup> (MFCs-III), respectively. V(V) and Cr(VI) were added in the form of  $\text{NaVO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , respectively. The conventional mass unit (mg L<sup>-1</sup>) was employed for easy comparison with previous research [2]. The electron acceptors were relatively abundant compared with the electron donors in present research to investigate the behaviors of the electron acceptors in the cathode compartment. The pH was adjusted with HCl (1:1). The metal concentration and the pH of the catholyte were selected considering the actual condition of vanadium containing wastewater [6].

### 2.3. Operation of the double chamber MFCs

The six MFCs had been well domesticated before the formal experiments as described in our previous research [2,6]. After the start-up, each MFC was replaced with new cathode electrode and fresh electrolytes, and then operated to evaluate the reduction of V(V) and Cr(VI) and electricity generation, with the external resistance of 1000 Ω. During the operation, polarization curves were obtained to determine the maximum power generation. The environmental temperature for all the MFCs was kept at 30 °C by employing a water bath throughout the entire experiment as previous used [6]. The MFCs were operated in 240 h fed-batch mode as most of the glucose was consumed within that time. For each MFC, three cycles were carried out to confirm the obtained results were repeatable. The two MFCs in each group were operated under identical conditions respectively and the average results were recorded.

### 2.4. Chemical analytical methods

Chemical oxygen demand (COD) was measured based on oxidation using potassium dichromate in concentrated sulfuric acid for 2 h at 150 °C. A spectrophotometric method was chosen to measure the generation of V(IV) [3]. The V(V) reduction efficiency was determined as the ratio of the generated V(IV) (mg L<sup>-1</sup>) to the initial V(V) concentration (mg L<sup>-1</sup>). V(IV) was selected as a measure because it is more readily deposited and more stable than other species of vanadium such as V(III) and V(II) in practice. By adjusting the pH of the cathode effluent to 6, the generated deposits were determined by X-ray photoelectron spectroscopy (XPS) (Axis Ultra, UK). The concentration of Cr(VI) was determined using colorimetry, with 1,5-diphenylcarbazide employed as the color reagent in acidic solution [18]. Total vanadium and chromium were determined by ICP-MS (Thermo Fisher X series, Germany). pH was measured using a pH-201 meter (Hanna, Italy). The surface morphology of the cathodic electrode was examined using a scanning electron microscope (SEM) (Quanta, USA) after the entire test had been completed. Energy dispersive X-ray (EDX) analysis was also performed to identify the elemental composition of the deposits on the cathode surface.

### 2.5. Electrochemical monitoring and data representation

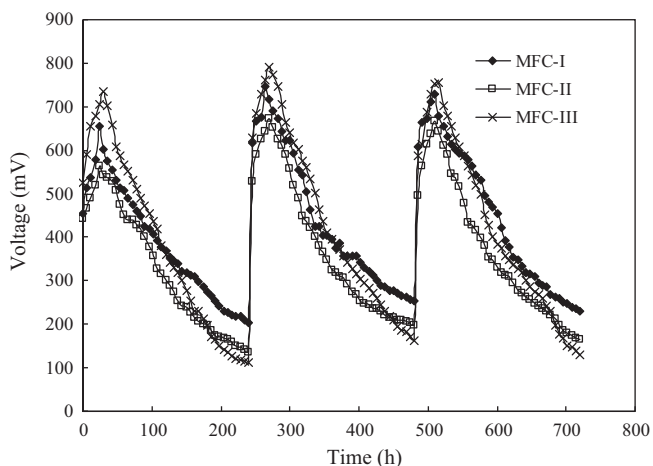
Open circuit voltage (OCV) and voltage outputs with the external resistance of 1000 Ω were measured at 5 min intervals throughout the test. Anodic and cathodic half-cell potentials were measured by placing Ag/AgCl reference electrodes in both compartments and were reported by normalizing to standard hydrogen electrode. Polarization curves were obtained by measuring voltage outputs of MFCs at various external resistances (ranging from 20,000 to 10 Ω) to evaluate the relationship between voltage and current.

Current ( $I$ ) was calculated for a given resistance ( $R$ ) from the voltage ( $V$ ) by  $I = V/R$ . Power ( $P$ ) was calculated by  $P = I \times V$  and normalized by the anode geometrical surface area (16 cm<sup>2</sup>). The coulombic efficiency (CE) was deduced from  $\text{CE} = C_p/C_T \times 100\%$ , where  $C_p$  is the total number of coulombs calculated by integrating the current over time, and  $C_T$  is the theoretical number of coulombs that can be produced from the used substrate (expressed in the form of COD).

## 3. Results and discussion

### 3.1. The OCV and the voltage output

With the new introduced cathode electrodes and electrolytes, the MFCs-I achieved a maximum OCV of  $997.2 \pm 23.8$  mV, and the similar results were also obtained in the MFC-II and MFC-III, a



**Fig. 1.** The voltage outputs for MFC-I, MFC-II, MFC-III respectively with 1000  $\Omega$  external resistance during the three cycles operation.

comparable value with previously reported for MFCs with Cr(VI) or V(V) as the sole electron acceptor, which was about 900 mV [19] or 1000 mV [2], respectively. This indicated that the MFCs in present study had been well developed and achieved the similar performance as reported in previous research [2,19].

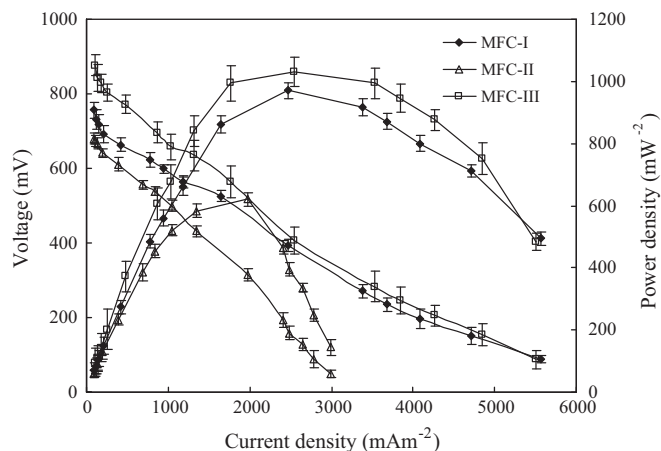
The voltage outputs for the MFCs operated with 1000  $\Omega$  external resistance during the operation were presented in Fig. 1. Three cycles were carried out and the results were presented to confirm the repeatability of the power output for each MFC in present study. It could be seen that the output voltages of the MFCs-I during the three cycles were between 200 and 750 mV, with the maximum value of approximately  $748.9 \pm 25.1$  mV. The voltage output obtained in MFC-I was promising when one considered previous research findings, in which the maximum voltage of 541 mV with 1000  $\Omega$  external resistance for double chamber MFC was obtained [20]. The higher voltage output of MFC-I could be attributed to the higher cathode potential. The cathode potentials were under the time-changing conditions and influenced by the concentrations of soluble oxidized and reduced species as well as the solution pH in our research. According to the Nernst equation, the theoretical potentials (mV) of both V and Cr redox reactions were presented as follows,

$$E_V = 991 - 118.4 \times \text{pH} \times \lg \frac{[\text{VO}^{2+}]}{[\text{VO}_2^+]} \quad (3)$$

$$E_{\text{Cr}} = 1330 - 138.1 \times \text{pH} \times \lg \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}]} \quad (4)$$

where  $[\text{VO}^{2+}]$ ,  $[\text{VO}_2^+]$ ,  $[\text{Cr}^{3+}]$  and  $[\text{Cr}_2\text{O}_7^{2-}]$  are the concentrations of the different types of ions in solution.

The actual cathode potentials of MFC-I measured over the duration of the test ranged from  $775.8 \pm 7.4$  mV to  $405.7 \pm 22.5$  mV. The better performance in present study could be attributed to the relatively higher actual electrochemical redox potentials of V(V) and Cr(VI) at high concentration and low pH in our research according to the Nernst equation (Eqs. (3) and (4)), compared with the values of cathode potential from aerated solution and  $\text{K}_3\text{Fe}(\text{CN})_6$  solution (both less than 400 mV), which were commonly used in MFC research [10,21]. Moreover, the actual cathode potential of MFC-I was lower than the calculated result at the same point in time, due to the polarization caused by the cathode efficiency decrease because of the deposition of generated Cr(III). Additionally, the anode potential of the MFCs-I ranged from  $-347.8 \pm 8.9$  mV to  $-209.5 \pm 23.7$  mV during the operation, which was compatible with previous studies [10,21]. Moreover, the voltage outputs of the



**Fig. 2.** The polarization curves and power outputs obtained for the three groups of MFCs. The values were obtained by measuring voltages across various external resistances (ranging from 10 to 20,000  $\Omega$ ).

three groups of MFCs gradually decreased during the operation due to the depletion of electron donors in the anode compartment.

In another aspect, it could be found from Fig. 1 that the voltage outputs of MFC-I were much higher than those of MFC-II, indicating that the cathode potential was improved by replacing part of V(V) with Cr(VI), compared with our previous finding [2]. Moreover, the voltage outputs of MFC-I declined relatively slower referring to MFC-III (Fig. 1), illustrating the generated Cr(III) from Cr(VI) reduction attached on the cathode surface and affected the electricity generation efficiency. This effect had been reported before [22] and more significant in the MFC-III as the concentration of initial Cr concentration was much higher in MFC-III than MFC-I. The whole results proved that the voltage outputs could be enhanced by employing the two electron acceptors together, compared with V(V) as the sole electron acceptor, while the cathode efficiency decrease because of the generated deposits from Cr(VI) reduction process could also be mitigated, indicating that vanadium containing wastewater was a promising electron acceptor in MFC application.

### 3.2. The polarization curves investigation

Polarization curves were obtained with closed-circuit MFCs at the period of the highest voltage output (Fig. 2). The highest power output of MFC-I was  $970.2 \pm 20.6$   $\text{mW m}^{-2}$  at a current density of  $2462.5 \pm 23.1$   $\text{mA m}^{-2}$ , which was higher than  $570$   $\text{mW m}^{-2}$  attained in the cathode-aerated double chamber MFCs [23]. Differences in solubility and mass transfer between the two types of electron acceptors (oxygen and high-electrochemically active metal ions) could influence power generation. V(V) and Cr(VI) had similar standard electrochemical redox potentials with oxygen, but their solubility was much greater than oxygen, thus lowering the mass transfer resistance and making electron acceptors abundantly available in the cathode electrolyte. It should be noted that oxygen transfer resistance was often the main factor affecting the MFC performance [24].

In addition, the metal ion that had relatively higher electrochemical redox potential acted as electron acceptor in present research. The actual redox potential of Cr was relatively higher than that of V at the beginning in our present research, so Cr(VI) was consumed and reduced first as electron acceptor. With the concentration of Cr(VI) decreasing and Cr(III) depositing, the electrochemical redox potential of V(V) exceeded that of Cr(VI) and began to act as electron acceptor. Cr(VI) might become electron acceptor again with V(V) being consumed. This competition might

appear repeatedly and V(V) and Cr(VI) acted as electron acceptor alternatively.

The maximum power density of MFCs-II was  $620.2 \pm 14.7 \text{ mW m}^{-2}$  at a current density of  $1968.8 \pm 19.3 \text{ mA m}^{-2}$ , which was consistent with the result of  $572 \text{ mW m}^{-2}$  by employing V(V) as the sole cathode electron acceptor in MFCs, reported by Zhang et al. [2]. This value obtained in MFC-II was lower than that of MFCs-I due to the relatively lower actual electrochemical redox potential of V(V) compared with Cr(VI). Alternatively, the maximum power density of MFC-III was  $1030.2 \pm 30.7 \text{ mW m}^{-2}$  at a current density of  $2537.5 \pm 46.3 \text{ mA m}^{-2}$ , which was compatible with that reported by Wang et al. [19], who employed Cr(VI) as the sole cathode electron acceptor in MFCs. Moreover, the variance of the maximum power density acquired in the MFC-III was much larger than that in the MFC-I. Actually, about 2.3% decrease of the maximum power density of MFC-III was obtained during the three-cycle operation, compared with 1.5% decrease for MFC-I. This was caused by relatively larger amount of generated Cr(III) that attached on the cathode surface and affected its efficiency in the MFC-III, referring to the MFC-I.

The CE of MFC-I based on COD was about  $25.8 \pm 5.7\%$ , similar to that for conventional MFCs employing glucose as fuel and for MFC-II ( $27.4 \pm 6.6\%$ ) and MFC-III ( $23.3 \pm 8.2\%$ ), which indicated that the present MFCs were well developed and could successfully harvest energy from artificial organic wastewater. The pH of the anolyte decreased less than 1 unit (from 7.00 to  $6.27 \pm 0.09$ ) during the operation because of the addition of phosphate buffer solution, which would cause little affect on the anode microbes and confirm the long-time operation of our proposed MFCs. It could be concluded that MFCs equipped V(V) and Cr(VI) as joint cathode electron acceptors could improve the power output with relieving the cathode efficiency decrease, compared with V(V) or Cr(VI) as sole electron acceptor. It should be mentioned that the power outputs of the MFCs-I were not high enough for directly actual application at present, further efforts should be made to improve the power outputs or electricity accumulation by connecting the MFC in series or in parallel for actual application of MFC technology in vanadium containing wastewater treatment as well as energy recovery in the future.

### 3.3. V(V) and Cr(VI) reduction in MFCs

In the cathode compartment of the MFCs-I, V(V) and Cr(VI) acted as electron acceptors alternately to receive the electrons from the anode compartment and themselves were reduced. The variable quantities of gibbs free energy for both Eqs. (1) and (2) based on glucose were calculated and both of them were less than zero, indicating that both the reactions could go on spontaneously. Fig. 3 showed that the concentrations of V(V) and Cr(VI) in MFC-I decreased gradually with time during the 240 h operating period. At the end of the 240 h operating period, reduction efficiencies were achieved of  $67.9 \pm 3.1\%$  for V(V) and  $75.4 \pm 1.9\%$  for Cr(VI). The Cr(VI) reduction efficiency was comparable with previous research where  $100 \text{ mg L}^{-1}$  Cr(VI) with initial pH 2 could be completely removed during 150 h with Cr(VI) acting as the sole electron acceptor [19]. And this efficiency could be improved by increasing the area of the PEM as reported by Li et al. [22]. The V(V) reduction efficiency decreased slightly when compared with the result obtained from the MFCs with V(V) acting as sole electron acceptor [2]. Electrons from anode were consumed for Cr(VI) reduction first as the actual electrochemical redox potential of Cr(VI) was relatively higher than that of V(V) in present study. The deposits generated from Cr(VI) reduction might attach on the cathode surface and affect the V(V) reduction subsequently. The anolyte was also monitored after the operation and few vanadium or chromium was detected because of the relatively small area of PEM (about  $4 \text{ cm}^2$ ). From Fig. 3 it

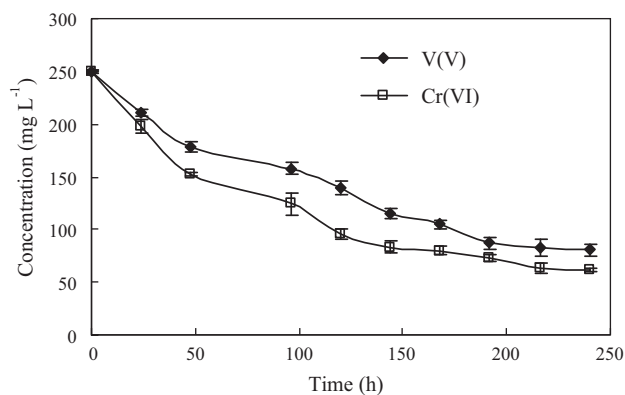


Fig. 3. Time histories of V(V) and Cr(VI) concentrations in the catholyte during the 240 h operating period of the MFC-I during the 240 h operating time.

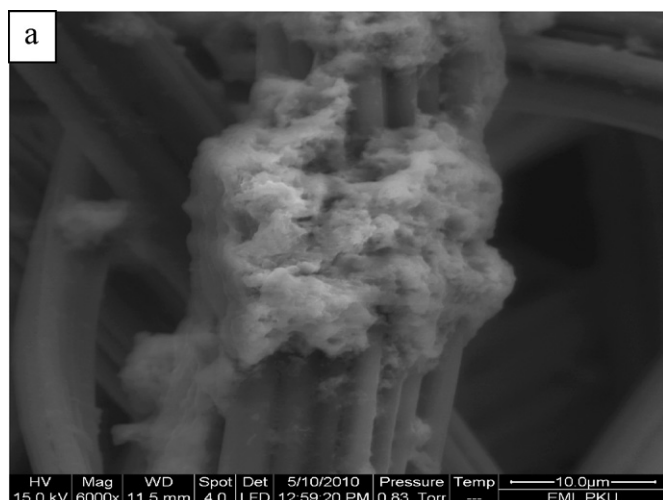
could also be seen that Cr(VI) was reduced more quickly than V(V). The metal which had higher electrochemical redox potential in the cathode environment acted as electron acceptor and itself was reduced during the operation of the MFCs. The actual redox potential of Cr(VI) was relatively higher than that of V(V) under the condition with the same concentration, pH and temperature, thus the electrons could be transferred to Cr(VI) more conveniently for its reduction.

Turning to another aspect, V(V) is the most toxic of the species of vanadium. After reduction V(V) converted to V(IV), which is less toxic and can be easily treated by downstream processes. This would be discussed in the following section of this research. The present study demonstrated that V(V) could be reduced successfully in the cathode compartment of double chamber MFCs. At present, the conventional method to treat Cr(VI) is to reduce it by chemical or electrochemical means into non-toxic Cr(III). The MFC technology presented herein was essentially based on this reduction concept, and had the advantage over other biological treatment processes in that it could simultaneously generate electricity while having a higher Cr(VI) concentration tolerance, especially the wastewater contained little organic matter for microbe growth [19]. For the above reasons, certain pollutants in vanadium containing wastewater, such as V(V) and Cr(VI), are satisfactorily reduced and handled by MFCs. However, it should be noted that there were still residual metal ions in the wastewater. Future research is needed on how to remove heavy metals from the aqueous solution in order to solve the vanadium containing wastewater problem in its entirety.

### 3.4. Study of deposits on the cathode surface

After the 240 h operating period,  $15.3 \pm 2.7\%$  of total vanadium and  $44.8 \pm 1.8\%$  of total chromium were removed from the catholyte in the MFC-I, indicating that a portion of the heavy metals had been extracted from the liquid phase. Deposits were observed by SEM (Fig. 4a) on the cathode surface of the double chamber MFCs, demonstrating the decrease in total metals. Using EDX technology (Fig. 4b), it was found that the deposits mainly consisted of chromium, with small amount of vanadium and without no other nonmetallic elements, illustrating that most of the reduction product of Cr(VI) namely Cr(III) had deposited on the cathode surface while hardly any V(IV) had separated out. This was consistent with the observation that Cr(III) oxide deposits only dissolve in the cathode medium when the solution  $\text{pH} < 1$  [22]. In this study, the pH of the catholyte gradually increased from 2.00 to  $3.76 \pm 0.27$  with the operation of the MFCs. The generated Cr(III) existed in the form of hydroxide, according to the chromium pe-pH relationship

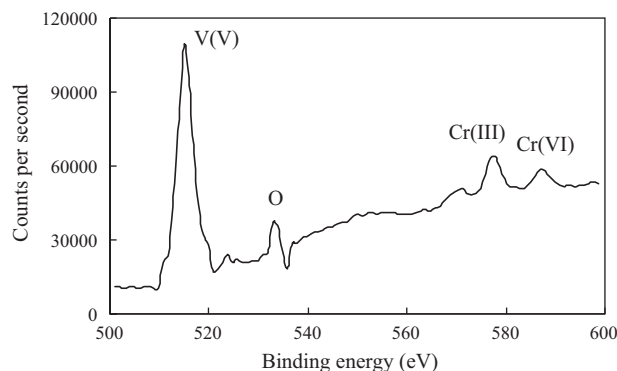




**Fig. 4.** SEM image and EDX spectra for the cathode surface of the MFC-I (a) the deposits attached to the cathode surface (6000 $\times$ ); (b) the EDX spectra for the aforementioned deposits.

diagram [25]. The solubility product constant ( $K_{sp}$ ) of  $\text{Cr}(\text{OH})_3$  is very small ( $6.3 \times 10^{-31}$ ) under the experimental temperature, thus  $\text{Cr}(\text{III})$  would precipitate from the catholyte after its generation. Moreover, EDX spectra were obtained for the cathode electrode before the batch mode experiments commenced. Carbon was the only element detected, indicating that the cathode was initially heavy metal free, whereas heavy metals were observed on the cathode surface at the end of the test period. It was anticipated that metals especially chromium could also be recovered from the cathode surface, thus solving toxicity problems caused by the presence of  $\text{Cr}(\text{VI})$  in vanadium containing wastewater as well as recovering energy simultaneously. Additionally, the performance of the cathode electrode in the aspects of energy recovery and  $\text{V}(\text{V})$  reduction might be affected by the deposition of  $\text{Cr}(\text{III})$ , which could be inferred from the MFC-III, as relatively larger amount of deposits were attached on the cathode surface and its efficiency decreased accordingly, compared with MFC-I. Effective methods based on ultrasound or acid dissolution should be exploited to clean the deposits conveniently and recover the cathode efficiency in our following research.

In the present tests, hardly any ( $3.8 \pm 0.9\%$ ) vanadium was precipitated because of the solubility change caused by the pH rise in the cathode compartment during the 240 h operation. Although  $67.9 \pm 3.1\%$  of  $\text{V}(\text{V})$  had been reduced to  $\text{V}(\text{IV})$  during the MFC-I operation, most vanadium remained in the catholyte and should be removed and recovered from the solution.



**Fig. 5.** XPS analysis of the deposits generated by adjusting the pH of the exhausted catholyte to 6. The deposits were concentrated using a mixed cellulose filter membrane.

### 3.5. The exhausted catholyte precipitation

After 240 h operation of the MFCs, the exhausted catholyte mainly contained deliquescent vanadium, most of which had been reduced from  $\text{V}(\text{V})$  to  $\text{V}(\text{IV})$ . In practice, the deliquescent metal ions must also be removed in order to complete the wastewater treatment. The pH of the exhausted catholyte in MFC-I rose from 2.00 to  $3.76 \pm 0.27$  during the 240 h operation. Noting that  $\text{V}(\text{IV})$  has minimum solubility at a pH of 6 [26], the exhausted catholyte of MFC-I was adjusted to a pH of 6 by adding  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (1:1). Many exiguous particles appeared immediately, suspended in the solution. They were enriched from the solution by passing three times through a syringe filter with  $0.22 \mu\text{m}$  – pore-size membrane unit. The color of the enriched particles gradually darkened in air. The enriched particles were of  $\text{V}(\text{IV})$ , which was re-oxidized to  $\text{V}(\text{V})$  by oxygen present in the air [2]. Fig. 5 presented the results of XPS analysis, applied to identify the chemical form of the enriched particles. The peak number of counts per second occurred at a binding energy of 515.9 eV, indicating that  $\text{V}(\text{V})$  was the main constituent of the deposits. As the binding energy of deposits for the exhausted catholyte in MFC-II during the same process was 517.2 eV, pointing to pure  $\text{V}(\text{V})$ . Only a small quantity of chromium was detected in the deposits for the exhausted catholyte in MFC-I, perhaps due to the change in solution pH or to possible reactions. In practice,  $\text{V}(\text{V})$  could be also recovered from this process, instead of being merely removed from the aqueous solution, which offered a promising method for valuable metal recovery.

After precipitation, the concentrations of total vanadium and total chromium in the filtrate of MFC-I were  $97.8 \pm 8.1 \text{ mg L}^{-1}$  and  $71.5 \pm 7.5 \text{ mg L}^{-1}$ , indicating the removal efficiencies of total vanadium and total chromium reached  $60.9 \pm 2.5\%$  and  $71.4 \pm 1.7\%$ , respectively. These results were promising for chromium containing wastewater treatment in comparison with previous findings [19,22]. Accordingly, it could be concluded that MFC based technologies are beneficial for vanadium containing wastewater treatment as well as vanadium and chromium recovery with electricity generation. In another aspect, there were also vanadium and chromium ions left in the exhausted catholyte after the precipitation, other traditional physical or chemical methods should be considered to be combined with MFC technology to treat vanadium containing wastewater completely before discharge. Attention should also be paid to combine MFC technology with traditional methods to improve the energy and valuable metals recovery with effective treatment vanadium containing wastewater in the future.

## 4. Conclusions

$\text{V}(\text{V})$  and  $\text{Cr}(\text{VI})$  are pollutants commonly found in vanadium containing wastewater. By employing vanadium containing

wastewater as the cathodic electron acceptor, simultaneous reduction of V(V) and Cr(VI) with electricity generation has been successfully achieved in double chamber MFCs. The operating principles of MFCs with two different electron acceptors were also investigated and discussed in present research. The maximum voltage outputs of the MFCs was  $970.2 \pm 60.5 \text{ mW m}^{-2}$ , which was enhanced with mitigating the electrode efficiency reduction by employing the two electron acceptors together, compared with only the sole (V(V) or Cr(VI)). After reduction, chromium was mainly deposited on the cathode surface in the form of Cr(III) oxides, while vanadium was mostly precipitated and recovered from exhausted catholyte by adjusting pH, realizing the removal efficiencies of total vanadium and total chromium as high as  $60.9 \pm 2.5\%$  and  $71.4 \pm 1.7\%$ , respectively.

### Acknowledgements

Financial support is gratefully acknowledged from the Fundamental Research Funds for the Central Universities (2011YYL109). The authors are grateful to Prof. Alistair Borthwick from University of Oxford for his kind help in English editing. The authors would like to thank the editor and the anonymous reviewers for their constructive suggestions.

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