A laminar flow microfluidic fuel cell for detection of hexavalent chromium concentration

Dingding Ye,^{1,2} Yang Yang,^{1,2} Jun Li,^{1,2} Xun Zhu,^{1,2} Qiang Liao,^{1,2,a)} and Biao Zhang^{1,2}

¹Key Laboratory of Low-Grade Energy Utilization Technologies and Systems (Chongqing University), Ministry of Education, Chongqing 400030, China

²Institute of Engineering Thermophysics, Chongqing University, Chongqing 400030, China

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An electrochemical hexavalent chromium concentration sensor based on a microfluidic fuel cell is presented. The correlation between current density and chromium concentration is established in this report. Three related operation parameters are investigated, including pH values, temperature, and external resistance on the sensor performance. The results show that the current density increases with increasing temperature and the sensor produces a maximum regression coefficient at the catholyte pH value of 1.0. Moreover, it is found that the external resistance has a great influence on the linearity and current densities of the microfluidic sensor. Owing to the membraneless structure and the steady co-laminar flow inside the microchannel, the microfluidic sensor exhibits short response time to hexavalent chromium concentration. The laminar flow fuel cell sensor provides a new and simple method for detecting hexavalent chromium concentration in the industrial wastewater. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

Wastewater containing hexavalent chromium is discharged from plating, leather tanning, and wood preservation industries.^{1–4} The Cr(VI) concentrations in wastewater produced by these industries are estimated to be between 0.1 and 200 mg l⁻¹.⁵ For instance, the Cr(VI) concentrations in wastewater from chrome tanning plant, electroplating plant, and tannery plant are 3.7 mg l⁻¹,⁶ 1.0 mg l⁻¹,⁷ and 8.3 mg l⁻¹,⁸ respectively. Due to the highly toxic and carcinogenic effect on human and animal health of the dissolved Cr⁶⁺,^{9–11} it is essential to detect the concentration of soluble Cr⁶⁺ in the industrial wastewater at these levels.

Up to now, various chemical and physical methods have been reported to detect Cr⁶⁺ concentrations in the ambient air¹² or in the solution.^{13,14} The determination of Cr⁶⁺ in the ambient air is mainly via alkaline impregnated filters. For the soluble Cr⁶⁺ detection, the most commonly used technique is spectrophotometry relied upon the formation of a colored complex between Cr⁶⁺ and 1,5-diphenylcarbazide (DPC). Recently, atomic absorption spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) are also presented to detect Cr⁶⁺.^{15–18} Table I compares major features of current detection techniques. As summarized in Table I, these methods clearly suffer from several disadvantages such as time consuming, expensive materials, and difficulty in realizing *in situ* or remote area with low power supply.

Laminar flow fuel cell (LFFC), also called membraneless microfluidic fuel cell, is a relatively new type of micro fuel cell utilizing characteristics of fluid in low Reynolds (*Re*) number regimes (less than 2100). Unlike the conventional micro fuel cells with a proton exchange membrane,^{19,20} a liquid-liquid interface acting as the virtual membrane is developed by co-flowing laminar streams of fuel and oxidant in a microchannel.^{21,22} During the past decade or

^{a)} Author to whom correspondence should be addressed. Electronic mail: lqzx@cqu.edu.cn. Tel./Fax: +86 023 65102474.

TABLE I. Summary of major features of Cr⁶⁺ detection techniques.

Type of detection	Response time	Detection range	Device	Main material	Reference
Surface enhanced Raman scattering	NA	<10 000 ppm	Self-assembled monolayer	Gold colloidal particles	Mosier-Boss and Putnam ¹³
Electroanalytical sensing	100–200 s	0.2–520 mg l ⁻¹	Self-assembled screen-printed electrodes	Al ₂ O ₃ , Ag, graphite	Miscoria <i>et al.</i> ¹⁴
Electrothermal atomic absorption spectrometric [ET-AAS]	50 s [85–120 °C]	<0.01 µg l ⁻¹	Atom absorption spectrometer + Autosampler	Nano particle TiO ₂	Wu <i>et al.</i> ¹⁵
Electrochemical detection by	20–40 s	0.025–2.6 mg l ⁻¹	Self-assembled modified ITO electrodes	Nano particle Au	Tsai and Chen ¹⁸

so, the LFFC has attracted much attention because the simple architecture eliminates the membrane-related problems including membrane degradation and water management.²² Recently, the LFFC has opened up new opportunities to detect the electrochemical activity of microorganisms benefited from its short hydraulic retention time, fast response time, and high energy output.^{23,24} Therefore, compared with the traditional detection methods of Cr⁶⁺, laminar flow fuel cells may provide an alternative, simple, and low-cost approach to the detection of the Cr⁶⁺ concentration.

In the present study, a sensor based on an LFFC to detect Cr⁶⁺ concentrations is reported. The current density response to the stepped variation in Cr⁶⁺ concentrations is recorded and a linear relationship between the current density and Cr⁶⁺ concentrations is established. To simulate the potential operation conditions, the effects of external resistance, pH values and temperature on the sensor performance are investigated in detail. Finally, the stability test is conducted to analyze the possibility to be a practical application.

II. MATERIALS AND METHODS

A. Fuel cell construction

A schematic of the LFFC sensor was shown in Fig. 1. The LFFC sensor was comprised of a microchannel and two polymethylmethacrylate (PMMA) plates (10 mm thick) with two inlets and one outlet. A 40 mm long and 2 mm wide microchannel was constructed by the graphite plates placed side by side as our previous study^{25,26} showed. In the microchannel, the anolyte (formic acid) and catholyte (hexavalent chromium) flowed in parallel without convective mixing. In order to separate the inlet channels of the two streams and seal the microchannel, two PMMA (1 mm thick) flakes were horizontally put on the both ends of the microchannel. To immediately catalyze the reaction of formic acid, the island-structural Pd catalysts with a loading of 5 mg cm⁻² were repeatedly electrodeposited on the anode followed by Nafion coating.²⁷ On the cathode, the graphite plate with no catalyst directly acted as the electrode. The LFFC sensor was held together by six M4 screw joints and placed in a water tank to maintain the stable temperature.

B. Fuel cell characterization

Reactants were prepared by dilution in the deionized water. The fuel and oxidant were formic acid (1 M) and potassium dichromate, respectively. The electrochemical reaction at the anode is²⁸

The primary Cr⁶⁺ reduction in an acid medium is given by

FIG. 3. Feasibility testing: (a) CV of the electrodes in 0.5 M H_2SO_4 at a scan rate of 10 mV s^{-1} . (b) Individual electrode polarization and power density curves.

the current was obtained until a steady state was reached. Cyclic voltammetry (CV) was also performed by the electrochemical workstation in 0.5 M H_2SO_4 in the potential range 0.0 V–0.9 V at a scan rate of 10 mV s^{-1} . In the following tests, voltages (U) were recorded by an Agilent 34970 data acquisition unit. Current (I) can be calculated via Ohm's law and output power density (P) by the equation: $P = U \times I/A$, where A was the surface area of the electrode. Current and power densities were normalized to the anode area (0.4 cm^2).

III. RESULTS AND DISCUSSION

A. Cell performance

A feasibility test is conducted for illustrating the principle of the LFFC sensor. First, the difference between electrode morphologies is displayed by the electrode surface SEM images as shown in Fig. 2. As illustrated in Fig. 2(b), Pd catalysts are uniformly distributed on the anode surface. By contrast, only rough graphite morphology is observed on the cathode surface (Fig. 2(a)). For further demonstrating the catalytic activity, CV results of the anode and cathode are displayed in Fig. 3(a). An anodic sharp hydrogen desorption peak centered at 0.06 V (vs. SHE (standard hydrogen electrode)) is observed, which indicates the existence of palladium catalyst on the anode surface. This typical hydrogen desorption profile is in agreement with the previous reports.^{29,30} On the other hand, resulting from no catalyst deposited on the cathode surface, no obvious peak can be observed from the CV result. The cell performance test is then carried out by chronoamperometry under stepwise potentiostatic control and the result is shown in Fig. 3(b). 1 M formic acid and $50 \text{ mg l}^{-1} \text{ Cr}^{6+}$ solutions are fed into the anode and cathode, respectively. A maximum power density of 0.025 W m^{-2} is generated from the LFFC. More importantly, the individual potential curve shows the anode potential increases slightly, while the cathode potential drops significantly. It strongly suggests that the cell performance depends largely on the cathodic potential losses rather than the anodic performance, even though the LFFC is operated at a high Cr^{6+} concentration (50 mg l^{-1}). Therefore, it can be deduced that the cathodic potential may drop more significantly at Cr^{6+} concentrations lower than 50 mg l^{-1} correlated to more serious mass transport limitation. At this point, this LFFC is expected to be used to detect Cr^{6+} by cathodic potential or current density.

B. Response of current generation to different Cr^{6+} concentrations

The response of current generation to Cr^{6+} concentrations is shown in Fig. 4(a). It can be clearly seen that the response current density shows stepwise variation with increasing Cr^{6+} concentrations. The mean response time is less than 1 min to reach a steady state when the Cr^{6+} concentration is changed in the catholyte. Importantly, the capability of short response time is essential to the success of developing a high-performance sensor. The good sensitivity to the short hydraulic retention time (HRT) is due to the fast electrochemical reaction rate in the microfluidic fuel cells.^{31,32} Fig. 4(b) shows a linear relationship between the current density

FIG. 4. (a) Time course of current generation at different Cr^{6+} concentrations. (b) Relationship between current density and Cr^{6+} concentrations. Operation condition: temperature, 20 °C; pH, 1.0; and R, 10 000 Ω .

and Cr^{6+} concentration. It can be clearly seen that the current density increases linearly from $15.87 \mu\text{A cm}^{-2}$ to $24.52 \mu\text{A cm}^{-2}$ with increasing Cr^{6+} concentrations from 1 mg l^{-1} to 10 mg l^{-1} , which confirms that the LFFC can be used as a sensor to detect the Cr^{6+} concentration. It can be easily understood by the fact that the high Cr^{6+} concentration increases the reaction rate on the cathode. Besides, the regression coefficient is 0.97 suggesting that the LFFC sensor shows an excellent performance in all Cr^{6+} concentrations. The sensor performance is studied further under various conditions in Secs. III C–III E.

C. Sensor performance with different external resistances

In practical applications, the LFFC sensor normally works under a certain external loading. Therefore, the sensor performance is explored by varying the external resistance from 2000 Ω to 10 000 Ω . In all tested external resistances, as shown in Fig. 5, the linear regression coefficient is higher than 0.97 and varies with changing the external resistance. It is interesting to note that when the external resistance is 2000 Ω or 5000 Ω , the sensor exhibits good linearity at Cr^{6+} concentrations higher than 2.5 mg l^{-1} . However, a great deviation in Cr^{6+} concentration measurement is observed at low Cr^{6+} concentrations ($< 2.5 \text{ mg l}^{-1}$) at 2000 Ω or 5000 Ω associated with the high parasitic current density. Because when the mass density of formic acid is substantially higher than the catholyte, the side-by-side flow structure will be distorted and a

FIG. 5. The effect of external resistance on Cr^{6+} measurement. Operation condition: temperature, 20 °C; pH, 1.0.

FIG. 6. The effect of pH (a) and temperature (b) on the LFFC sensor performance. Operation condition: R, 10 000 Ω ; temperature, 20 $^\circ\text{C}$ (not applicable for Fig. 6(b)); and pH, 1.0 (not applicable for Fig. 6(b)).

high parasitic current will be produced.³³ Although a higher current is generated at a lower resistance, higher resistance would result in a slower reaction rate and could reduce the influence of Cr^{6+} consumption on the monitoring activity.³⁴ This result indicates that the external resistance dominates the low limit of the sensor. Therefore, it is clear that the external resistance has a notable impact on the sensor performance. Based on the above results, 10 000 Ω is selected as the external resistance in the following experiments.

D. Effect of pH values and temperature on the sensor performance

According to reactions (2) and (3), pH values and temperature play important roles in the electrochemical reaction at the cathode as well as the sensor performance. Meanwhile, pH values and temperature are two crucially controllable factors in the real wastewater detection. Therefore, the effects of pH values and temperature on the sensor performance are shown in Fig. 6. A linear relationship between current density and Cr^{6+} concentrations is observed at all the pH (1.0, 3.3, 6.8, and 8.5) conditions. At pH value of 1.0, a regression coefficient of 0.97 at all Cr^{6+} concentration conditions is obtained due to the enhanced cathode reduction efficiency at a high proton concentration. However, in other cases, a large deviation in 1 mg l^{-1} can be observed. Furthermore, the current density shows a little difference at pH value of 1.0. For a certain Cr^{6+} concentration, the current density in alkaline media is higher than those in acid media, which can be credited to the enhanced proton transfer to the cathode in the alkaline media.^{35,36}

Then, the interaction between current density and Cr^{6+} concentrations at different temperature (20 $^\circ\text{C}$, 40 $^\circ\text{C}$, 50 $^\circ\text{C}$, 60 $^\circ\text{C}$) is investigated. As shown in Fig. 6(b), when temperature is increased from 20 $^\circ\text{C}$ to 60 $^\circ\text{C}$, the current density at Cr^{6+} concentration of 10 mg l^{-1} is boosted almost by 30% (from $24.5 \mu\text{A cm}^{-2}$ to $35 \mu\text{A cm}^{-2}$). However, it is noteworthy the liner regression coefficient is simultaneously decreased with the increasing temperature. This result may be ascribed to the fact that the formic is easily evaporated when the temperature is higher than 40 $^\circ\text{C}$. Meanwhile, the diffusion rate is increased due to the high temperature and the reactants mixing would consequently be aggravated. The destructive flow-flow interface could cause a large deviation especially under the low detected concentration. Considering the poorest linear regression coefficient of 0.84 is obtained in relatively high temperature, room temperature is well-suited to the LFFC sensor.

E. Sensor stability

In order to characterize the stability of LFFC sensor, a long time continuous test is conducted at 5 mg l^{-1} and 10 mg l^{-1} Cr^{6+} concentrations, as shown in Fig. 7. Once the external resistance (10 000 Ω) is connected, the current density reaches a stable status and exhibits a fast response to this change. Meanwhile, it is found that the current density of the LFFC sensor

FIG. 7. Stability test of LFFC sensor (background current has been deducted). Operation condition: temperature, 20 °C; R, 10 000 Ω; pH, 1.0; and Cr⁶⁺ concentrations, 5 mg l⁻¹ and 10 mg l⁻¹.

operated under 5 mg l⁻¹ shows a neglectable fluctuation (the maximum fluctuation is less than 1 μA cm⁻²) during the 4 h test. However, a much larger fluctuation in the current density under 10 mg l⁻¹ is observed (inset in Fig. 7). The possible reason is a cross-over aggravation at a high catholyte concentration. An unfavorable mixed potential causes an unstable electricity generation. In brief, the significantly stable characteristic during the whole test indicates its functionality of be using in the industrial wastewater containing soluble Cr⁶⁺.

IV. CONCLUSIONS

In this study, a LFFC is first proposed as a sensor to detect hexavalent chromium concentrations. The low-cost, energy-efficient LFFC can be produced through a simple fabrication process and the corresponding capital cost is obviously lower than those for other conventional testing methods. The experimental results demonstrate a linear current generation as a function of hexavalent chromium concentrations. Less than 1 min response time is obtained by the novel sensor. In particular, the sensor performance under different working conditions is evaluated, including pH values, temperature, and external resistance. Small error bars in all conditions show excellent reproducibility of quantitative measurements. Considering the large deviation of small dose of Cr⁶⁺, 2.5 mg l⁻¹ is recognized as the lowest detection limit. The LFFC sensor provides a new and simple pathway for quantitative monitoring of hexavalent chromium concentrations in the industrial wastewater, but long term studies on the real contaminated water are still needed.

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