Performance of tetramethoxyphenyl porphyrin cobalt(II) (CoTMPP) based stainless steel cathode in the electricigenic permeable reactive barrier for groundwater organic contamination remediation

Shi-Kun Zhu, Bin Fan, Jie-Wei Wu, Yuan-Yuan Feng and Yun Zhang

ABSTRACT

An electricigenic permeable reactive barrier (EPRB) technology was brought forward for remediation of organic-contaminated groundwater, with a benefit that it overcame the limitations of electron acceptor addition in other groundwater remediation methods. To investigate performances of constructions and materials used in EPRB system, several kinds of reactors were designed and prepared in laboratory. Stainless steel wires, a kind of nontoxic, inexpensive and conductive material, were used as basic material of electrode. In order to improve cathodic oxygen reduction capability, a cathode based on tetramethoxyphenyl porphyrin cobalt (II) (CoTMPP) was prepared and studied in this paper. Results showed that a high catalytic activity for oxygen reduction was exhibited by the CoTMPP based cathode, with an electricity generation 3 times as high as that of the naked stainless steel cathode. Some evidence indicated that by loading on the surface of stainless steel wires and heat-treated under anaerobic conditions, epoxy resin, with its curing agents, might have got a catalytic capability for oxygen reduction.

Key words | carbon nanotube, electricigenic permeable reactive barrier, groundwater remediation, organic contamination, porphyrin cobalt(II) (CoTMPP), stainless steel cathode

Shi-Kun Zhu
Bin Fan (corresponding author)
Jie-Wei Wu
Yuan-Yuan Feng
Yun Zhang
State Key Laboratory of Environmental Aquatic Chemistry,
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences,
P.O. Box 2871,
Beijing 100085,
PR China
E-mail: fanbin@rcees.ac.cn

INTRODUCTION

Organic contamination of groundwater is becoming a critical problem over the whole world. Due to the unacceptable rate of natural attenuation of organic contaminations and high energy consumption of traditional pump-and-treat method, in situ bioremediation technologies are gradually considered to be a better choice for groundwater remediation contaminated by organic chemicals and have a great development.

In situ treatment of organic chemicals by biological means is a technology that encourages growth and reproduction of microorganisms which are capable of degrading the chemicals (Testa & Winegardner 2000). For biodegradation of organics to be successful, it is

necessary to provide a continuous supply of a suitable electron acceptor, such as oxygen or nitrate. The methods used to provide electron acceptor for microorganisms include air sparging, (pure) oxygen injection, peroxide addition, nitrate addition, etc. Every strategy has its strengths and weaknesses. Air sparging may be the most economical method, but some kinds of organic contaminations, such as gasoline (Yaniga & Smith 1984) and trichloromethane (Nyer 1985), can not be degraded at a desired rate for the low concentration of dissolved oxygen. Dissolved oxygen concentration can be greatly increased (up to 40 ~ 50 mg/L) in groundwater by pure oxygen injection, whose application is seriously limited before the

preparation technology have been improved. Compared with the direct oxygen supply method, it is quite a different strategy for electron acceptor additions that peroxides (hydrogen peroxide (Hinchee & Olfenbuttel 1991), calcium peroxide (Liu *et al.* 2006; Cassidy & Irvine 1999) etc) decomposes or reacts with water to produce oxygen. However, as well as their instability and costliness, peroxides have harmful effects on organisms contacting them for their inhabitation or toxicity (Cassidy & Irvine 1999), so there will be some security risk when using them. Nitrate, another electron acceptor that can be used by microorganisms (Hutchins *et al.* 1991), is one of the groundwater contaminations needed to be controlled, so before introducing them, a question must be answered: which do you want, the organic pollution or a nitrate pollution? In one word, it is a key problem in in-situ groundwater bioremediation technology to develop a safe, reliable and economical method to provide electron acceptor continuously for microorganisms.

Electricigens are a type of microorganism discovered in recent years. They exhibit a novel form of respiration (Greer 2007). Instead of transferring electrons to soluble oxidative substances when breaking down organic matters, they transfer electrons to outside insoluble matter such as iron(III) oxides, Mn(IV)oxides etc.. This behavior makes them proficient at transferring electrons to another electron acceptor, an electrode, by which electrons can follow an electric circuit to the terminal electron acceptor, oxygen in most cases. Based on this mechanism, an electricigene permeable reactive barrier (EPRB) was proposed for remediation of organic contaminated groundwater (Figure 1). An EPRB consists of two main units. The underground unit is made of a material that is electron conductive, water permeable, and microbial affinitive. It is set up at a cross section of the contaminated groundwater flow. On the surface of the material, anodophilic biofilm is cultivated. The near-ground unit is made of cathodic oxygen reductive material, and it is set up where oxygen supplement is convenient. The two units are linked both by wire and by water. The whole system is like a biofuel cell. The underground unit acts as the anode, on which organic pollutants can be completely oxidized to CO_2 by the biofilm. The electrons are accepted by the anode and then transferred to the cathode, on which oxygen acts as the final electron

Figure 1 | Schematic diagram of electricigene permeable reactive barrier (EPRB).
① cathode unit (aeration systems), ② anode unit (permeable reactive barrier).

acceptor and is reduced to OH^- . The benefit of the EPRB is that it overcomes the limitations of electron acceptor addition in the other groundwater remediation ways.

In order to investigate and test performances of constructions and materials used in EPRB system, several kinds of reactors, in which capability of a certain unit was designed as controlling factor, were prepared in laboratory. In this study, the research focus was on the performance of cathode unit in oxygen reduction capability, with a reactor system similar to that used in microbial fuel cells (MFCs) study. The methodology and technology in MFCs study (Gojkovi *et al.* 1999; Gojkovi *et al.* 2005; Logan *et al.* 2006a) were also used for references. As well as the catalytic activity for the oxygen reduction reaction (ORR), environmental-friendliness, inexpensiveness and high-density-filled performance are crucial for EPRB cathode units, which is different from the MFCs systems.

To meet the challenge of the EPRB cathode materials, stainless steel wires were employed. After being twisted into spherical shapes, stainless steel wires have got the characteristics of permeability and larger specific surfaces and volume concentrations than common electrode materials, such as graphite sheets/foils, carbon papers and so on. Thanks to all the excellent performances, stainless steel wires have a future in in-situ groundwater remediation for a wide use.

As lack of catalytic activities for ORR, stainless steel wires need to be modified electrochemically to enhance capacities as an EPRB cathode. Technologies of

modification based on porphyrin cobalt (II) (Logan 2005; Zhao *et al.* 2005; Logan 2006), a widely studied method with a finer loading performance for oxygen reduction catalysis, were used in our study. Electrochemical measurements and the reactor described above were employed to determine the products.

MATERIALS AND METHODS

EPRB Reactor set-up and operation

A two-chamber EPRB reactor was built to test the performance of the CoTMPP-based stainless steel materials as an electrode catalyzing oxygen reduction (Figure 2). The two chambers with a proton exchange membrane (Liu *et al.* 2003) (PEM, 5 cm × 5 cm) at the middle each had a volume of 1.3 L. The anode chamber maintained a low oxygen atmosphere and were saturated with N₂ to expel oxygen before inoculated with the sediments from the Qinghe River (Beijing, China). In the cathode side, to keep high oxygen atmosphere air aeration were carried out. Anodic materials of the EPRB reactor were stainless steel wires with a mass of 20 g and cathodic materials were modified stainless steel wires, loaded with CoTMPP-based catalysts. The mass of the cathode was 5 g. Copper wires with a variable external resistance were employed to connect the anode and the cathode. To collect the signal of the circuit, a digital

multimeter (98A, VICTOR) was used. The EPRB reactor was placed on a shaking table. The shaking table concentrator kept running at a low speed during whole operations.

The EPRB reactor was fed a medium consisting of a phosphate buffer (300 mg/L), minerals (Logan 2005) (500 mg/L of NH₄Cl, 100 mg/L of MgCl₂, KCl and CaCl₂), vitamins and 1,000 mg/L of sucrose at the start up and 200 ~ 10,000 mg/L sucrose during the operation. NaHCO₃ was used to adjust the original pH to 7, and 1,000 mg/L of NaH₂PO₄ was used as the electrolyte in the cathodic chamber. All the chemicals above were purchased from Sinopharm Chemical Reagent Company, Ltd, China.

Catalyst and electrode preparation

CNT-supported CoTMPP catalyst preparation

The carbon nanotubes powder (Purity MWCNTs, Beijing Nanopowder Company) was first treated with hydrofluoric acid and nitric acid for 24 hours. After filtration and washing with deionized water, the black powder was dried at 80°C in a drying oven. The CoTMPP catalyst was prepared by dissolving 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphyrin cobalt(II) (Aldrich) in acetone, mixing with carbon nanotube powder, agitating the mixture using a magnetic stirrer for 24 h, and filtering rapidly through a nuclepore polycarbonate membrane. The solid samples were then heat treated in a horizontal tube furnace at temperature 750°C for 2 h under continuous flow of purified nitrogen and allowed to cool under flowing nitrogen.

Electrode preparation

Three types of electrodes were adopted as cathode in this study, including the naked stainless steel wire electrode, the Carbon Nanotube-Epoxy Resin-stainless steel wire electrode (ER electrode) and the CNT-CoTMPP-Epoxy Resin-stainless steel wire electrode (CoTMPP electrode). The naked stainless steel electrode was obtained by soaking purchased stainless steel wires in methanol: acetone (1:1) for 4 hours and then in HF: HNO₃ (2%:30%) for 30 s (Bergel *et al.* 2005). The ER electrode was prepared by binding carbon nanotubes onto the stainless steel wires with epoxy resins, and then treated under a certain temperature.

Figure 2 | EPRB reactor in study. (1) cathode, (2) air aeration system, (3) anode, (4) passage for sampling and feeding, (5) PEM. Load & SCS is Load and Signal Collection System.

The details of procedure were as follows: 0.1 g of carbon nanotube powder was mixed with silane coupling agent, 0.5 g of epoxy resin (WSR6101, Wuxi Blue Star Company) and 0.5 g of polyamide curing agent (Wuxi Blue Star Company), stirring and ultra sonicating for 20 min. The resulted mixture was pasted on the stainless steel wires, drying in an oven at 150°C for 2 hours. The precursor was then heat treated at 750°C for 30 min in a quartz tube. Before the heat-treated procedure, the quartz was evacuated and refilled with nitrogen. The CoTMPP electrode was produced using the same procedure as the ER electrode, except that the CNT-supported CoTMPP catalyst powder was used instead of the carbon nanotube powder.

Electrochemical measurements

Internal resistance determination

The internal resistance consisting of activation resistance, ohm resistance and concentration resistance was determined by recording polarization curves of the EPRB reactor (Hoogers 2003). A polarization curve represents the voltage as a function of the current (density). A variable resistance box was used to set variable external loads with a digital multimeter collecting electric signals. Using a periodical decrease of the load, the voltage was measured and the current was calculated using Ohms law. The external resistance decreased from 90,000 Ω to 10 Ω with a step range from 10,000 Ω to 10 Ω . The current and potential values were recorded 5 minutes after the external load varied, when the pseudo-steady state had been established (Logan *et al.* 2006b).

Cyclic voltammetry

An electrochemical workstation (CHI660C, Shanghai Chenhua Instrument Company) branched to a PC was used for cyclic voltammetry at a scan rate of 50 mV/s in the potential range of -600 mV to 600 mV (vs. Ag/AgCl). The working electrode was a CoTMPP-based stainless steel foil (2.5 cm $\times$ 2.5 cm) and the counter electrode was a platinum sheet (1 cm $\times$ 1 cm). An Ag/AgCl/KCl electrode (sat., Shanghai Precision and Scientific Instrument Company) was used as reference. For comparison a naked stainless steel foil (1 cm $\times$ 1 cm) was also introduced as the

working electrode. The electrolyte in working solution was 0.2 mol/L of NaH_2PO_4 , the same chemical as that in the cathode chamber of EPRB reactor. Oxygen was saturated before tests were conducted.

RESULTS

Cyclic voltammograms

Cyclic voltammetry curve was plotted to examine the performance of the CoTMPP-based stainless steel electrode on catalyzing oxygen reduction, by comparing with a naked electrode. Figure 3 showed that the electricity output of the CoTMPP electrode was much larger than that of the naked one in the scan range of -0.6 V to 0.6 V (vs. Ag/AgCl), especially during the range of 0 to 0.6 V, a output 10 times as large as the naked obtained, indicating a catalytic activity in oxygen reduction was gained by stainless steel sheets on which a CoTMPP-based catalyst was loaded.

Performance in EPRB reactor

Start-up and operations of EPRB reactor

1.3 L of suspension inoculated with sediments of the Qinghe River (1.25 L of medium with 50 mL sediments) was cultured for one week under anaerobic condition before it was transferred into the anodic chamber. After installation

Figure 3 | Cyclic voltammograms of naked stainless steel electrode (a) and CoTMPP-based stainless steel electrode (b) in 0.2 mol/L NaH_2PO_4 solution. Each electrode has a size of 25 mm $\times$ 25 mm. The electrode potential was swept at 50 mV/s from 0.6 V to -0.6 V and then back to 0.6 V (vs. Ag/AgCl).

Figure 4 | Start-up period (a) and cyclic running (b) of EPRB reactor, with a external resistance of 100 Ω .

of the electrode materials and the air aeration system, external circuits were connected to start up the EPRB reactor. The current was continuously recorded with a multimeter, as was shown in Figure 2. The current decreased sharply at the beginning of the operation, kept

stable at the low position around 400 μA for about 30 h and then gradually went up to about 1,600 μA . The steady output for more than 40 hours around 1,600 μA indicated the end of the reactor startup. The startup of the EPRB reactor lasted about 48 hours, which was much less than 7 days reported in MFCs papers, possibly caused by the pre-cultivation of the suspension.

After startup, operations of the EPRB reactor could enter the long-term cycles or short-term cycles (Figure 4b) by controlling the HRT of the medium and the dosing quantity of carbon source.

Internal resistance of EPRB reactor

The internal resistance (R_{int}) is a comprehensive parameter for assessment and characterization of the reactor construction, operation conditions, microbial status and capabilities of electrodes, and it is also a critical factor in electricity generation. The polarization curve was obtained (Figure 5a) by representing the voltage measured with a multimeter as functions of the current, which was calculated using Ohm's law. A linear fitting was applied to the data and the linear correlation coefficient was 0.9986, indicating that the polarization curve of the reactor could be described in a linear model and ohm resistance was the major among three types of the resistances. From the slope of the fitting curve an internal resistance of 279.1 Ω was determined, a little larger than the data reported and set the electricity generation limit of the EPRB reactor in internal-resistance-controlled mode. Under the control of R_{int} the electricity generation reached its theoretical limit when

Figure 5 | Polarization (a) and power (b) curves of EPRB reactor operating on sucrose. A linear polarization curve was obtained, which resulted in an internal resistance of 279 Ω .

external resistance R_{ex} was 0, calculated as

$$I_{\text{max}} = \frac{\text{OCV}}{R_{\text{int}}}$$

OCV is Open Circuit Voltage

An optimization of reactor construction and operation conditions should be conducted to reduce the values of R_{int} for a higher current density, and a better basis could be provided for investigation of cathode capability.

A power curve represented as a function of the current was showed in Figure 5b. The power output of the reactor increased first and then declined as the current output went up. Maximum power of 0.35 mW was obtained when the external resistance was adjusted equal to the internal resistance.

Electricity generation

Performance of the CoTMPP-based electrode was tested using the EPRB reactor by comparing the current output of CoTMPP-based stainless steel electrode and the naked electrode. A variable external resistance, whose values were 279 Ω , 100 Ω and 0 for each electrode, was employed during the experiment. Whether epoxy resins and polyamide curing agents, which was used as binders in CoTMPP electrode preparation, evolved a catalytic activity for oxygen reduction reaction during the heat-treated process was investigated using a ER electrode.

Figure 6 | Current generation of EPRB reactors employing different cathodes, (a) naked stainless steel cathode and (b) CoTMPP-based stainless steel cathode. Both cathodes had a mass of 5 g. External resistance of the circuits (1) $R_{\text{ex}} = 279 \Omega$; (2) $R_{\text{ex}} = 100 \Omega$; (3) $R_{\text{ex}} = 0$.

Table 1 | Power output of EPRB reactors with different cathodes

Power output (mW) cathode	External resistance (R_{ex})	
	100 Ω	279 Ω
CoTMPP electrode	0.332	0.340
ER electrode	0.215	0.218
Naked electrode	0.081	0.087

The maximum average currents of CoTMPP-naked and naked electrodes are shown in Figure 6. When the external resistance was 279 Ω , the current of the CoTMPP electrode was 1.9 times as strong as the value of the naked one, and the ratio increased to 2.1 and 2.95 with the external resistance declined to 100 Ω and 0, demonstrating that the application of the CoTMPP electrode in the EPRB reactor had obviously improved the cathode performance, and a higher efficiency will be achieved when using a lower external load in the circuit. When the external resistance was 0, the maximum current using a CoTMPP electrode reached 3.25 mA.

Using an ER electrode as the cathode of the EPRB reactor, the maximum average current could reach 1.6 times as large as the current using a naked electrode, almost 80% as the CoTMPP electrode, demonstrating that a catalytic activity for oxygen reduction reaction was obtained by the ER electrode through a heated-treated process. Thanks to inexpensive materials and uncomplicated procedures, the method applied to prepare ER electrodes may have a hopeful future.

The excellent performances of the CoTMPP electrode and the ER electrode were shown more obviously by a comparison of the power output (Table 1) than that of current output with the naked electrode. In the conditions of $R_{\text{ex}} = 100 \Omega$, the power output of the CoTMPP electrode was 4.1 times, with ER electrode 2.7 times, as large as that of the naked electrode.

CONCLUSIONS

The stainless steel wire electrode based on heat-treated porphyrins cobalt (II) with epoxy resins as binders has a high catalytic activity for oxygen reduction in the EPRB reactor, with evidence showing that when using a lower

load, a higher efficiency will be achieved. Typically, in conditions the external resistance was zero, the maximum electricity generation with a CoTMPP-based electrode as cathode reached 3.25 mA, almost 2 times larger than that using a naked electrode.

Some evidences indicated that a material of epoxy resin with its curing agents might have got a catalytic capability for oxygen reduction by loading on the surface of stainless steel and heat-treated under anaerobic conditions. Further work needs to be continued to illustrate the mechanism of catalytic activity generation and optimize the operation conditions to improve oxygen reduction efficiency.

ACKNOWLEDGEMENTS

This work was supported by National Natural Science Foundations of China (20777088 and 50538090).

REFERENCES

- Bergel, A., Féron, D. & Mollica, A. 2005 Catalysis of oxygen reduction in PEM fuel cell by seawater biofilm. *Electrochem. Commun.* **7**(9), 900–904.
- Cassidy, D. P. & Irvine, R. L. 1999 Use of calcium peroxide to provide oxygen for contaminant biodegradation in a saturated soil. *J. Hazard. Mater.* **69**(1), 25–39.
- Gojkovi, S. L., Gupta, S. & Savinell, R. F. 1999 Heat-treated iron (III) tetramethoxyphenyl porphyrin chloride supported on high-area carbon as an electrocatalyst for oxygen reduction part II. Kinetics of oxygen reduction. *J. Electroanal. Chem.* **462**(1), 63–72.
- Gojkovi, S. L., Gupta, S. & Savinell, R. F. 2005 Heat-treated iron (iii) tetramethoxyphenyl porphyrin supported on high-area carbon as an electrocatalyst for oxygen reduction. *J. Electrochem. Soc.* **145**, 3493.
- Greer, D. 2007 Harnessing the power of microbes. *Biocycle* **48**(5), 49.
- Hinchee, R. E., & Olfenbuttel R. F. 1991 *In Situ Bioreclamation: Applications and Investigations for Hydrocarbon and Contaminated Site Remediation*, Butterworth-Heinemann, Boston, USA.
- Hoogers, G. 2003 *Fuel Cell Technology Handbook*. CRC Press, Boca Raton, FL, USA.
- Hutchins, S. R., Downs, W. C., Wilson, J. T., Smith, G. B., Kovacs, D. A., Fine, D. D., Douglass, R. H. & Hendrix, D. J. 1991 Effect of nitrate addition on bioremediation of fuel-contaminated aquifer: field demonstration. *Ground Water* **29**(4), 571–581.
- Liu, F., Yi, B., Xing, D., Yu, J., Hou, Z. & Fu, Y. 2003 Development of novel self-humidifying composite membranes for fuel cells. *J. Power Sour.* **124**(1), 81–89.
- Liu, S. J., Jiang, B., Huang, G. Q. & Li, X. G. 2006 Laboratory column study for remediation of MTBE-contaminated groundwater using a biological two-layer permeable barrier. *Water Res.* **40**, 3401–3408.
- Logan, B. 2005 Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell. *Environ. Sci. Technol.* **39**, 658–662.
- Logan, B. 2006 Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells. *Environ. Sci. Technol.* **40**, 364–369.
- Logan, B. E., Hamelers, B., Rozendal, R., Schrder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W. & Rabaey, K. 2006a Microbial fuel cells: methodology and technology. *Environ. Sci. Technol.* **40**(17), 5181–5192.
- Logan, B. E., Hamelers, B., Rozendal, R., Schrorder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W. & Rabaey, K. 2006b Microbial fuel cells: methodology and technology. *Environ. Sci. Technol.* **40**(17), 5181–5192.
- Nyer, E. K. 1985 *Groundwater Treatment Technology*. Van Nostrand Reinhold Company, New York. pp. 188.
- Testa, S. M. & Winegardner, D. L. 2000 *Restoration of Contaminated Aquifers: Petroleum Hydrocarbons and Organic Compounds*. CRC Press, Boca Raton, FL, USA.
- Yaniga, P. M. & Smith, W. 1984 Aquifer Restoration via Accelerated In Situ Biodegradation of Organic Contaminants. pp. 451–470.
- Zhao, F., Harnisch, F., Schrder, U., Scholz, F., Bogdanoff, P. & Herrmann, I. 2005 Application of pyrolysed iron (II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. *Electrochem. Commun.* **7**(12), 1405–1410.