

# Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells

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## Abstract

The performance of iron(II) phthalocyanine (FePc) and cobalt tetramethoxyphenylporphyrin (CoTMPP) based oxygen reduction catalysts was studied in view of the application as cathode materials in microbial fuel cells. Galvanostatic and potentiostatic experiments were performed in order to compare the proposed materials to platinum and hexacyanoferrate(III) based systems. Additionally, two-chamber microbial fuel cell experiments were carried out to demonstrate that the transition metal based materials are well suitable to fully substitute the traditional cathode materials in microbial fuel cells.

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## 1. Introduction

The recent interest in microbial fuel cells (MFCs) can be attributed to the endeavour of gaining access to the direct generation of electricity from biomass and waste [1–3]. Very different approaches have been developed to facilitate the electron transfer between microorganisms and the MFC anodes [4–6]. Thus, biofilm based MFCs have recently received much attention as they allow the highly beneficial combination of COD removal and electricity generation from waste water [2,5,7,8]. An approach that we are following in our lab are hydrogen mediated microbial fuel cells based on heterotrophic, photo-heterotrophic as well as purely photosynthetic microbiological activity [9–14].

Most efforts in the past have almost exclusively been devoted to the development of the MFC anode, whereas the cathode has been rather neglected. Only recently, increasing efforts have been made in developing new concepts for microbial fuel cell cathodes [15]. As the cathode materials usually platinum based oxygen electrodes [15,16] or, more often, ferricyanide served as an experimental electron acceptor (e.g. [17]). The latter material suffers from its inability to be regenerated (re-oxidised) by oxygen or air, which consequently requires a periodical replacement of the exhausted catholyte solution. Platinum, however, as an excellent oxygen reduction catalyst, should be ruled out for microbial fuel cell application due to its high price.

The development of oxygen reduction catalysts for fuel cell application represents a major research field, and a wealth of information is available on the mechanisms of the electrochemical oxygen reduction (see, as one example [18]) and potential oxygen reduction catalysts (e.g. [19,20]). Increasing efforts have been made to develop inexpensive

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non-noble metal electrocatalyst. An emphasis are biomimetic approaches utilising transition metal porphyrines and phthalocyanines (e.g. [21]). These materials are known to be good oxygen reduction catalysts that represent inexpensive alternatives to platinum (e.g. [22]). Jasinski and coworkers [23] were the first to report that transition metal porphyrines and phthalocyanines show an electrochemical activity towards the oxygen reduction reaction and can be used as cathode catalyst in fuel cells. The molecules have planar structures with the metal ion symmetrically surrounded by four nitrogen atoms, which leads to the common term transition metal  $N_4$  macrocycles. Jahnke et al. [24] improved the stability as well as the electrochemical activity of transition metal porphyrins deposited on a carbon support by a pyrolytic heat treatment step in the range from 450 to 900 °C in an inert atmosphere. In contrast to the precursor these centres are bonded to a conducting carbon matrix after the heat treatment. Since that time numerous efforts have been made to clarify the structure of the catalytic centre and to improve the electrochemical performance [25–31]. Beside the state of the catalytic centres, the morphology of the final catalyst material strongly influences the electrochemical activity. Originally, the catalysts are prepared by impregnation of a carbon support with the porphyrines or phthalocyanines. In [32], a new preparation method with structure forming substances (outgassing auxiliary agents) has been reported which provokes a highly porous CoTMPP based electrocatalyst. The addition of outgassing auxiliary agents, like metal oxalates, leads to a foaming process during the pyrolysis of CoTMPP. Additionally, solid decomposition products of the oxalate (metal and oxides) form a framework embedded within the pyrolysis product which is removed by a subsequent acid treatment. Finally, a highly porous carbon matrix with embedded centres is obtained. With this procedure electrochemical activities (determined in RDE measurements in 0.5 M  $H_2SO_4$  at 0.5 V vs. Ag/AgCl) have been achieved close to that of commercial 20% Pt/C (Etek) the oxygen reduction.

Electricity generation in microbial fuel cells is based on the metabolic activity of living microorganisms. This fact requires that such fuel cell systems have to run under conditions predefined by the optimum growth and living conditions of the utilised microorganisms. Thus, MFCs are usually operated at ambient temperature, atmospheric pressure and at pH neutral or only slightly acidic conditions. These prerequisites have to be taken into account for the selection of electrode materials. On the other hand, the current densities of microbial fuel cells are rather low, with maximum reported values of 1.5 mA  $cm^{-2}$  [9], which does not necessarily require the use of high-performance catalysts.

For this communication we have chosen two different oxygen reduction catalysts, based on pyrolysed carbon-supported iron(II) phthalocyanine (FePc) and cobalt tetramethoxyphenylporphyrin (CoTMPP) foamed with iron oxalate, for application as cathode materials in two-chamber

microbial fuel cells. We demonstrate that these materials are well suitable for MFC application, allowing sufficiently high current densities, high open circuit potentials as well as a high stability.

## 2. Experimental

### 2.1. Catalyst preparation

*Iron(II) phthalocyanine (FePc) based catalyst:* 2 g FePc was dissolved in tetrahydrofuran (THF) at room temperature, afterwards the mixture was added to a dispersion of 2 g carbon nanoparticles (Vulcan XC-72) in THF, and was treated in an ultrasonic bath for 30 min. Finally, the THF was removed and subsequently the impregnated carbon nanoparticles were heat treated under argon gas at 700 °C for 2 h. Then this material was ball-milled for one hour.

*CoTMPP based catalyst:* 0.019 mol CoTMPP,  $8.2 \times 10^{-4}$  mol iron(II) oxalate and 0.002 mol elementary sulphur were thoroughly mixed in a mortar. The mixture was then heat treated under argon flow in a split-hinge furnace equipped with a quartz tube. The heat treatment was performed in a first step at 450 °C for 2 h and then in a second step at 750 °C for 1 h under continuous flow. Afterwards the catalyst was quenched to room temperature. Finally, it was conditioned 30 min in 1 M hydrochloric acid in order to remove catalytic inactive by-products. This preparation method is described in [32] and is patented [33].

### 2.2. Cathode preparation

The cathode material was either graphite foil (Chempur<sup>®</sup>, Karlsruhe, Germany) or carbon cloth (Toray, EC-CCL-060). The electrocatalyst was mixed with poly(tetrafluoroethylene) (Aldrich, 60% dispersion in water) in an ultrasonic bath, the mixture was then transferred onto the substrates and was allowed to dry at 80 °C overnight. The amount of catalyst was about 2 mg  $cm^{-2}$ . For the fuel cell experiments, a cathode was used with a geometrical surface area of 30  $cm^2$ . For the galvanostatic measurements, 1  $cm^2$  graphite foils were used. For comparison of the new materials with platinum, a platinum sheet was electrochemically platinised in a 50-mmol  $L^{-1}$   $H_2PtCl_6$  solution.

### 2.3. Anode preparation

For the fuel cell experiments a polymer modified platinum electrode served as the anode. For that, a platinum mesh electrode (100  $cm^2$  geometrical surface) was electrochemically platinised in a 50-mmol  $L^{-1}$   $H_2PtCl_6$  solution, then an overlay of the redox polymer poly(2,3,5,6-tetrafluoranyliline) was deposited as described before [11].

### 2.4. MFC test system set-up

For the MFC experiments we used *Escherichia coli* K12 as the biocatalyst [9]. *E. coli* were grown aerobically at

37 °C for 12–24 h in a standard medium containing 10 g glucose, 5 g yeast extract, 10 g NaHCO<sub>3</sub> and 8.5 g NaH<sub>2</sub>PO<sub>4</sub> per litre. The same medium served as the solution in the anode chamber. For the experiments 1 mL of an overnight culture was inoculated into fresh medium, then *E. coli* were cultivated in the anaerobic anode chamber.

The solution in the cathode chamber was 0.5 M NaH<sub>2</sub>PO<sub>4</sub>, the pH was adjusted to 3.3 by adding phosphoric acid. Air was purged into the cathode compartment in order to supply the oxygen needed for the electrochemical reaction.

The MFC experiments were carried out in batch mode using a self-made fuel cell model, which was composed of two 250 mL volume-bottom flasks pressed together at laterally inserted windows [13]. A Nafion 117 membrane of 2.2 cm diameter was clamped between the windows separating anode and cathode compartment. Both, anode and cathode chamber, contained a reference electrode (Ag/AgCl sat. KCl, 0.195 V vs. SHE) for independently measuring the individual electrode potentials. The MFCs were placed in a temperature-controlled chamber and run at 37 °C.

### 2.5. Electrochemical instrumentation

Cyclic voltammograms and galvanostatic linear sweep voltammetry were carried out in a conventional three electrode arrangement using Autolab systems (EcoChemie, Netherlands). The reference electrode was a Ag/AgCl (sat. KCl, Sensortechnik Meinsberg, Germany), a platinum sheet served as the counter electrode. These experiments were carried out at room temperature.

Current and potential measurements in the fuel cell experiments were carried out using a digital multimeter (Integra 2700 series equipped with 7700 multiplexer, Keithley Instruments, Inc., Cleveland, USA) interfaced to a personal computer. For the determination of the power output a variable resistance (0–5 kΩ) was used as the external load.

## 3. Results and discussion

Fig. 1 displays the cyclic voltammogram of a CoTMPP based catalyst modified graphite electrode in a phosphate buffer solution under oxygen bubbling, in comparison to the voltammogram of an unmodified graphite electrode. The figure clearly demonstrates the catalytic effect of the porphyrin catalyst on the oxygen reduction. Compared to the unmodified carbon electrode, the potential of the oxygen reduction is shifted by approximately 400 mV towards positive potential. Additionally, the reduction current increases significantly. FePc showed similar results, with a slightly more negative onset potential (0.4 V) than the Co based material (0.45 V) and a lower limiting current density (data not shown).

The dependence of the open circuit potential of the FePc and CoTMPP catalyst modified electrodes on the pH of an oxygen saturated solution is shown in Fig. 2. The figure shows that the potential of the CoTMPP electrode

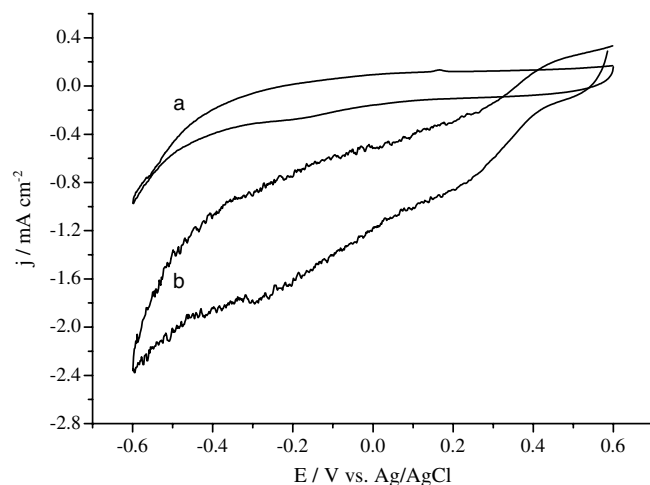


Fig. 1. Cyclic voltammograms of a graphite foil electrode (a) and a CoTMPP catalyst modified graphite foil electrode (b) in 0.5 M phosphate buffer solution, pH 3.3, under O<sub>2</sub> purging. Scan rate: 1 mV s<sup>-1</sup>. The geometrical surface area was 0.5 cm<sup>2</sup>.

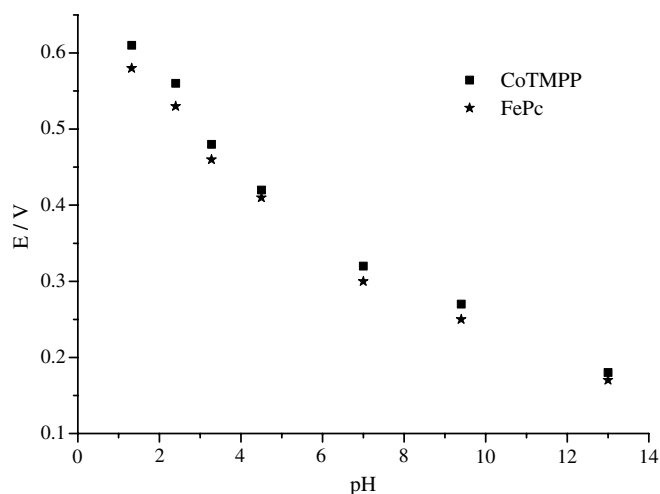


Fig. 2. Open circuit potentials of FePc and CoTMPP oxygen reduction catalyst modified graphite foil electrodes in phosphate buffer solution (0.5 M) as a function of the pH. The solutions were constantly purged with oxygen.

(480 mV at pH 3.3) lies slightly over that of the FePc modified electrode (460 mV, pH 3.3). At platinum, the OCP was 637 mV (data not shown). The expected reversible formal potential of the oxygen/water redox couple for the same experimental conditions is 790 mV. The considerably lower reduction potentials at CoTMPP and FePc electrodes still indicate an appreciable irreversibility, possibly also involving H<sub>2</sub>O<sub>2</sub> as a product. This is supported by preliminary rotating ring disk experiments at the discussed CoTMPP catalyst which show a hydrogen peroxide production of 7% at a potential of 0.5 V in 0.5 M H<sub>2</sub>SO<sub>4</sub>. A complete four electron oxygen reduction to water, however, has been already been reported for FePc (see, e.g. [34]).

Clearly visible in Fig. 2 are two sections – at pH values below seven a slope of 59 mV/pH is found, and above pH 7

the slope is 23 mV/pH. The different slopes indicate a change of the nature of the rate-determining step, most probably from a  $4e^-/4H^+$  (or  $2e^-/2H^+$ ) to a  $4e^-/2H^+$  (or  $2e^-/1H^+$ ) reaction (relative to one oxygen molecule).

Certainly, the strong shift of the oxygen reduction potential towards negative values with increasing pH leads to the desire to have the cathode operating at low pH. On the other hand, the anode compartment of microbial fuel cells generally runs at pH neutral or only slightly acidic conditions, as dictated by the conditions for the microbial growth. In order to avoid too strong pH gradients across the fuel cell membrane, a compromise needs to be found.

Fig. 3 shows the results of galvanostatic linear sweep polarisation measurements. This technique represents a convenient tool for the characterisation and evaluation of electrocatalysts for fuel cell and battery applications. In this figure, the dependence of the oxygen reduction potential on the current density at the different electrodes in *air saturated* electrolyte solution and in a ferricyanide solution is shown. As expected, the platinum black electrode showed the highest open circuit potential (0.59 V), followed by CoTMPP and FePc with 0.48 and 0.47 V, respectively. In the air saturated solution, the advantage of the platinum electrode vanishes at current densities above  $0.2 \text{ mA cm}^{-2}$ . At higher current densities, the polarisation curves of platinum, the CoTMPP and the FePc based electrodes are very close to each other, with CoTMPP being the best non-noble metal catalyst. This rather unexpectedly similar performance can probably be attributed to the low concentration of oxygen in the electrolyte when bubbled with air. This is supported by experiments in which pure oxygen was used to purge the solution. Here, the differences are slightly more pronounced. It can be expected that the performance

will differ more considerably when the electrodes are used in direct contact to air. For the application in microbial fuel cells, i.e., with current densities at the anodes currently reaching  $1.5 \text{ mA cm}^{-2}$  maximum [9] the achieved current densities are well acceptable. It has to be noted that at current densities up to  $0.7 \text{ mA cm}^{-2}$  of both, CoTMPP and FePc based electrode, are superior to the ferricyanide system (Fig. 3).

Figs. 4 and 5 show two sets of data of different MFC batch experiments. In Fig. 4, the course of the potentials ( $E_{\text{cell}}$ ,  $E_{\text{anode}}$ ,  $E_{\text{cathode}}$ ) at a constant external load of  $200 \Omega$  was recorded over time after the anode compartment was

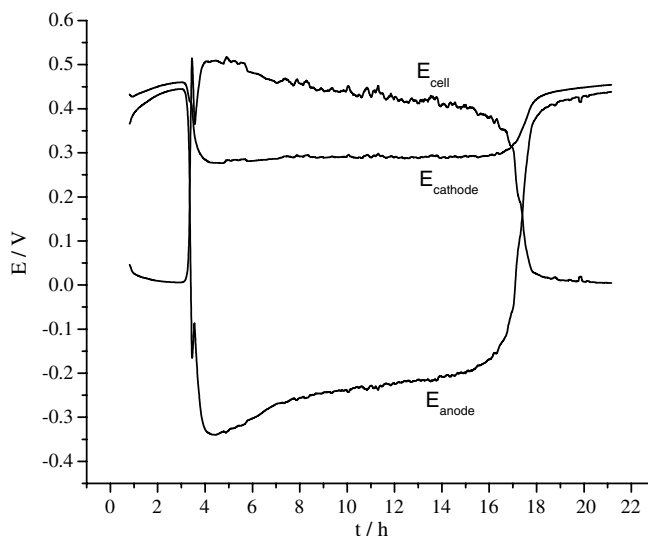


Fig. 4. Course of the individual potentials measured in an MFC experiment running under batch conditions. The anaerobic compartment was a freshly inoculated anaerobic culture of *E. coli K12* growing on glucose. The experiment was performed at a fixed external resistance of  $200 \Omega$ . The cathode was a FePc catalyst modified graphite foil electrode in  $0.5 \text{ M NaH}_2\text{PO}_4$ , pH 3.3. The cathode solution was purged with air.

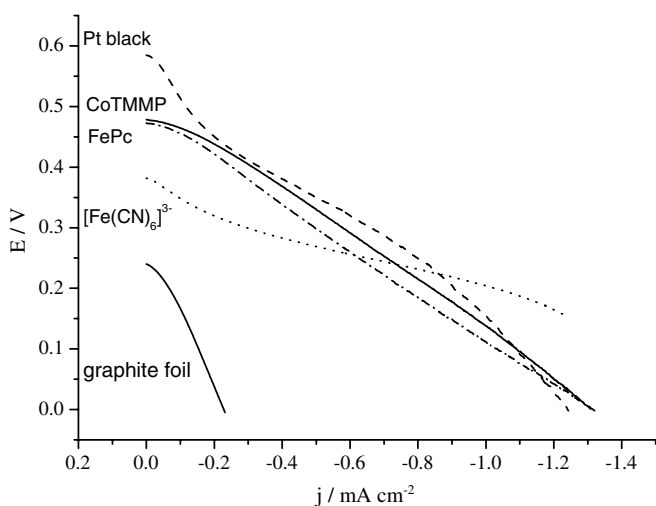


Fig. 3. Galvanostatic linear sweep voltammograms of different electrodes in *air saturated* solution ( $0.5 \text{ M NaH}_2\text{PO}_4$ , pH 3.3, solution was purged with air); scan rate  $10^{-5} \text{ A/s}$ . The working electrodes were: unmodified graphite foil, platinumised platinum, CoTMPP and FePc catalyst modified graphite foil. The ferricyanide system was measured at an unmodified graphite electrode under addition of  $50 \text{ mM K}_3[\text{Fe}(\text{CN})_6]$  to the buffer solution.

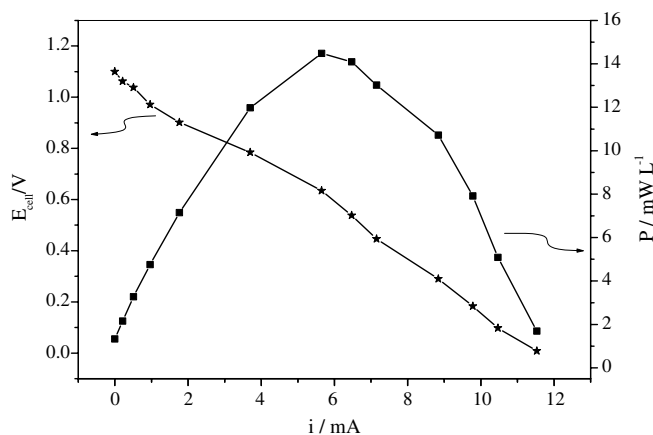


Fig. 5. Microbial fuel cell analysis: independent potential and current measurement at variable resistance between 0 and  $5000 \Omega$  in a MFC batch experiment as in Fig. 4. The left axis shows the cell potential as function of the current and the right axis represents the resulting power. The cathode was a CoTMPP catalyst modified carbon cloth electrode in  $0.5 \text{ M NaH}_2\text{PO}_4$ , pH 3.3. The cathode solution was purged with air.

Table 1  
Summary of model MFC experimental data<sup>a</sup>

	FePc-Cathode	CoTMPP-Cathode
Open circuit potential	1.07 V	1.10 V
Steady state current <sup>b</sup>	10.52 mA	11.53 mA
Maximum current <sup>b</sup>	14.31 mA	16.67 mA
Maximum power output	13.88 mW L <sup>-1</sup>	14.32 mW L <sup>-1</sup>

<sup>a</sup> Experimental conditions as in Fig. 5.

<sup>b</sup> Short circuit currents.

inoculated with living cells of *E. coli* K12. The anodic reaction was based on the in situ electrocatalytic oxidation of microbial hydrogen at the polymer modified platinum anode (see, e.g. [11]). The cathode was a FePc catalyst modified carbon cloth electrode. When the bacteria start growing (indicated by the steep drop of the anode potential after 3.5 h) the cell potential reaches a maximum value of about 0.51 V ( $i = 3.2$  mA), which slowly decreases to 0.36 V (2 mA) over the next 16 h, and then collapses due to substrate exhaustion. With the beginning of fermentation, the cathodic potential decreases to a value of 290 mV, remaining then practically constant over the course of the experiment, until the anode potential rises after 17 h. At this point the cathode potential returns to its starting value, showing that the activity of the catalyst has not faded. One and the same electrode was used for a series of experiments over days, not showing any sign of fatigue. Using CoTMPP based cathodes similar results were achieved (not shown).

Fig. 5 shows the polarisation and the power curve of the fuel cell system as a function of the measured steady-state currents at different external resistances. The open circuit potential of the FePc and CoTMPP cathode based MFCs were 1.07 and 1.10 V, respectively. In our previous studies using ferricyanide as the electron acceptor, the open circuit potential reached values of only 0.89 V. A comparison of MFC experiment results for FePc and CoTMPP cathodes are shown in Table 1. Under short circuit conditions the steady state current was 10.52 and 11.53 mA, respectively. The maximum power output of the FePc based MFC was 13.88 mW L<sup>-1</sup>, which corresponds to a current of 14.31 mA at the cell potential 0.62 mV. It certainly needs to be noted that the used fuel cell configuration is well suited for separately studying the anode and cathode behaviour, it is, however, not optimised for providing highest possible performance.

#### 4. Conclusions

The performance of FePc and CoTMPP based oxygen reduction catalysts was investigated in view of the application as cathode materials in MFCs. Under the chosen conditions of air saturated electrolyte solution these materials show results very similar to platinum oxygen electrodes. The performance of the cobalt based material is slightly better than that of the iron compound, which may be due to the more sophisticated preparation procedure. The

difference could, however, also be caused by a stronger back bonding between oxygen and cobalt – necessary for an efficient oxygen reduction catalysis [35]. The results prove that FePc and CoTMPP based oxygen cathodes are inexpensive and yet efficient alternatives for microbial fuel cell application. The results of this investigation indicate an excellent durability of the studied catalysts; however, additional tests of the long term stability are required. Further work is necessary to study the mechanisms of the oxygen reduction at the porphyrin and phthalocyanine catalysts more in detail and to optimise the performance of the system. One way to do so is the application of this class of oxygen reduction catalysts using open air cathodes in single chamber microbial fuel cell as it has been independently investigated and recently submitted by Logan and co-workers [36].

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