

Fluorinated polyanilines as superior materials for electrocatalytic anodes in bacterial fuel cells

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Abstract

In a recent communication we demonstrated that electrodes consisting of a platinum electrocatalyst covered by a conductive polymer like polyaniline are well suited to serve as anodes harvesting electricity in microbial fuel cells [Angew. Chem. Int. Edn. 42 (2003) 2880]. In this communication we show that the fluorinated polyanilines poly(2-fluoroaniline) and poly(2,3,5,6-tetrafluoroaniline) outstrip the parent compound polyaniline in their performance as an electrode modifier. Similar to polyaniline they improve the catalytic activity of platinum towards the oxidation of hydrogen, product of the anaerobic microbial metabolism. Compared to polyaniline the fluorinated polymers are superior in the protection of platinum from becoming poisoned by metabolic by-products. The high stability of poly(2,3,5,6-tetrafluoroaniline) towards microbial and chemical degradation makes this compound a highly promising candidate for applications in microbially aggressive environments like sewage or sewage sludge.

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1. Introduction

The recent interest in microbial fuel cells [2] can be attributed to the endeavour of gaining access to the direct generation of electricity from biomass and waste [3]. A number of microbial fuel cells have been proposed showing that electricity generation is possible even from unexpected energy sources like marine sediments [4–6], sewage water and sludge [7]. Up to date, however, microbially based fuel cells still suffer from an insufficient current and power density. Recently we demonstrated that composite materials consisting of platinum covered by a conductive polymer are well suited to serve as anodes in microbial fuel cells. With this approach it was possible to boost the power output of microbial fuel cells by more than one order of magnitude [1].

Here we show that fluorinated polyanilines (see also [8]) outstrip conventional conductive polymers in their

performance as an electrode modifier. They are superior in the improvement of the tolerance of platinum against poisoning, thus enhancing the catalytic activity of anodes. The high stability of polytetrafluoroaniline towards microbial and chemical degradation makes this compound extremely useful for applications in microbially aggressive environments like sewage or sewage sludge.

2. Experimental

2.1. Chemicals

2,3,5,6-tetrafluoroaniline (Acros Organics) and 2-fluoroaniline (Fluka) were used as purchased from the manufacturers. All other used chemicals were of analytical grade.

2.2. Electrochemical instrumentation and setup

All electrochemical experiments were carried out under potentiostatic control, utilizing a three electrode

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arrangement consisting of the working electrode, a sat. Ag/AgCl, sat. KCl (0.195 V vs. SHE) reference electrode and a counter electrode (platinum wire or a carbon rod electrode). The counter electrode was separated from the bacterial solution by a Nafion[®] 117 perfluorinated membrane. The experiments were conducted with μ -AutolabII, PGSTAT20 and PGSTAT30 Autolab systems (Ecochemie, Netherlands). The PGSTAT30 potentiostat was equipped with five additional array modules allowing the simultaneous investigation of up to six working electrodes in connection with one reference electrode and one counter electrode. Sealed and thermostated fermentation vessels (100 mL) served as electrochemical cells which hosted the fermentation medium and the electrodes.

2.3. Electrode materials

Platinum sheet electrodes (paddle-shaped, 7.5 × 20 mm, 0.5 mm thickness), contacted with a platinum wire, platinum wire electrodes, Ø 0.5 mm, 2 cm length and paraffin impregnated graphite electrodes (PIGE) [9] were used as working electrodes.

2.4. Electrode preparation

The deposition of the conductive polymer layers was performed by electrochemical polymerization. Depending on the target polymer the electro-polymerization was carried out as follows. The polymerization of aniline followed a standard literature procedure, i.e. it was achieved by potential cycling between -0.1 and 1.2 V from an aqueous solution containing 0.1 mol L⁻¹ H₂SO₄ and 0.1 mol L⁻¹ aniline (scan rate 0.1 V s⁻¹, 15 cycles) [10]. The oxidative electropolymerization of the fluorinated anilines was carried out at fixed potentials, for 1000 s, from aqueous solutions with the following composition. (i) Poly(2-fluoroaniline) (2FPA): 0.1 M 2-fluoroaniline, 0.1 M HClO₄ and 0.1 M NaClO₄. The polymerization potential was 1.3 V. (ii) Poly(2,3,5,6-tetrafluoroaniline) (TFPA): 50 mM tetrafluoroaniline in 2 M HClO₄, the polymerization potential was either 1.3 or 1.6 V.

2.5. Bacterial growths

Escherichia coli K12 was grown aerobically at 37 °C for 12–24 h in a standard medium containing 10 g glucose (Merck, for biochemistry), 5 g yeast extract (spray dried, autolyzed, Sigma), 10 g NaHCO₃ and 8.5 g NaH₂PO₄ (Merck, p.a.) per litre. The same medium served as the electrolyte solution in the chronoamperometric experiments. For electrochemical experiments 1 mL of an overnight culture was inoculated into fresh medium. By blocking the access of oxygen the bacteria were now cultivated under anaerobic, fermentative conditions.

2.6. Sewage sampling

Sewage samples for this investigation were taken from a local wastewater treatment plant. The samples were taken from the wastewater stream after it passed the mechanical treatment stage and were stored in sealed plastic containers (1–3 L) where they were kept strictly anaerobic.

2.7. Fermentation product analysis

The non-gaseous fermentation products of *E. coli* K12 were analyzed with high performance liquid chromatography. The HPLC was equipped with a Rezex[™] ROA-Organic Acid column in combination with the SecurityGuard[™] cartridge AJO-4490. The chromatograms were recorded at a column temperature of 55 °C, the detector was a differential refractometer. The quantification of the gaseous products CO₂ and H₂ was performed volumetrically, the separation of H₂ from CO₂ being achieved by absorption of CO₂ in NaOH. In accordance with literature [11,12] the composition of the fermentation products for the mixed acid fermentation of glucose by *E. coli* K12 was as follows (mole_(product)/mole_(glucose)): ethanol (0.6), formate (0.02), acetate (0.45), succinate (0.13), lactate (0.67), CO₂ (0.4), hydrogen (0.4).

3. Results and discussion

Under anaerobic conditions and in the absence of other inorganic electron acceptors microorganisms use fermentation to feed on organic matter. Due to the lack of an inorganic electron sink the substrate is cleaved into fragments that serve as an electron donor and fragments that serve as the electron acceptor. So, parts of the substrate become partially or fully oxidized, others become reduced. In the fermentation of carbohydrates beside a range of reduced organic compounds hydrogen can be formed, produced via the cleavage of formate by the enzyme formate-hydrogen lyase (mixed acid fermentation, *E. coli*) or via a ferredoxin-linked pathway (butanediol fermentation, *Clostridia*). So it is known from the literature for various strains of *E. coli* to produce between 0.43 [11] and 0.91 mole [12] of hydrogen during the mixed acid fermentation of one mole glucose. In order to use the microbially formed hydrogen for electricity generation it either has to be collected, cleaned and processed in an external hydrogen fuel cell, but it can also be oxidized in situ [13,14]. There are good reasons for in situ hydrogen exploitation. Thus it is reported that a great number of microorganisms need the hydrogen partial pressure to be kept at low level, else the hydrogen production would significantly decrease [15]. It is also reported that when hydrogen is removed from

the microbial medium (usually by bubbling with nitrogen) higher yields of oxidized compounds and lower yields of reduced organic products are formed indicating an increased hydrogen formation [16]. Thus electrochemical depletion of the microbially formed hydrogen could assist and potentially even enhance the production of hydrogen.

So far, platinum despite of its price is unmatched in its properties towards the electrocatalytic oxidation of hydrogen. However, the bare metal is not suitable to be used in a “dirty” environment like a fermenting bacterial medium. Its liability to poisoning would lead to a fast and complete loss of the electrocatalytic activity (see current trace, Fig. 1(a), curve A). In order to use platinum for in situ electricity generation it is essential to find means to protect the metal from becoming deactivated by the partially high levels of electrode poisoning fermentation by-products. As we have demonstrated recently [1] and as it can be derived from the current response B, Fig. 1(a), the combination of platinum with an overlay of polyaniline slows down this deactivation process. Most likely, this can be attributed to an increased tolerance of the electrocatalyst against poisoning as the result of the interaction of the electronic structure of the polymer with the precious metal surface [17–19]. In contrast to the bare platinum electrode an anodic current starts flowing with the beginning of fermentation. Due to a still insufficient protection of the electrode, however, the current density is limited to a value of $90 \mu\text{A cm}^{-2}$. In many cases the accumulation of fermentation products with time leads to an almost complete loss of the electrode activity. The deactivation can be illustrated with a potentiodynamic experiment in which the catalytic activity of the electrode as a function of the applied potential is tested before and after the electrode served as an anode in a fermenting glucose medium. A freshly prepared electrode, immersed into a fermenting bacterial growth medium, exhibits a high catalytic activity in a potential range between -0.1 and $+0.5$ V (Fig. 1(b), curve A). At more positive potentials the current decreases due to platinum oxide formation, leading to a decreased ability of the platinum surface to catalytically oxidize hydrogen. When the electrode is now poised at a potential of 0.2 V in order to simulate the presence of a fuel cell cathode, the current decreases with time. A potentiodynamic scan recorded after this experiment reveals that the electrode activity almost completely disappeared (Fig. 1(b), curve B).

Curve C and D, Fig. 1(a), show the current response of poly(tetrafluoroaniline) and a poly(2-fluoroaniline) modified platinum electrodes. With a maximum current density of $530 \mu\text{A cm}^{-2}$ (polytetrafluoroaniline) and $455 \mu\text{A cm}^{-2}$ (poly(2-fluoroaniline)) both electrodes are superior in their catalytic activity compared to the polyaniline modified electrode, the polytetrafluoroaniline modified electrode showing a gradually higher per-

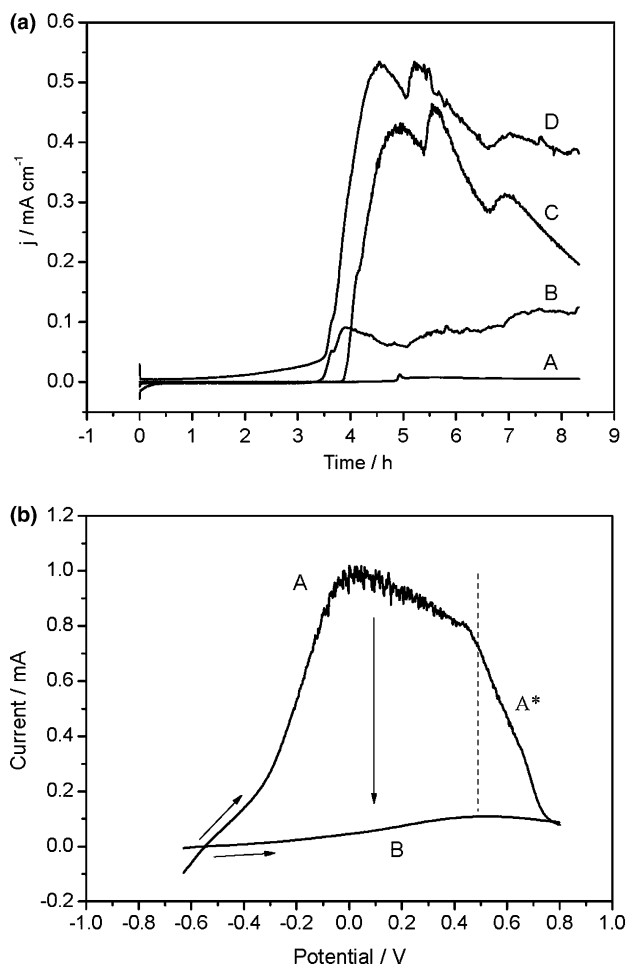


Fig. 1. (a) Current generation of a freshly inoculated anaerobic culture of *E. coli K12* in a standard glucose medium ($c_{\text{glucose}} = 0.55 \text{ mmol L}^{-1}$), measured at differently modified platinum electrodes. The electrodes were potentiostatically poised at a potential of 0.2 V vs. Ag/AgCl (sat. KCl). The experiment was carried out at 37 °C. A: unmodified platinum electrode; B: polyaniline modified Pt electrode; C: poly(2-fluoroaniline) modified Pt electrode; D: poly(tetrafluoroaniline) modified Pt electrode. (b) Linear sweep voltammetric response of a polyaniline modified platinum electrode (1 cm^2 surface area) placed in a stirred anaerobic culture of *E. coli K12* (conditions as above). The scan rate was 5 mVs^{-1} . The voltammograms were recorded during the stationary phase of the anaerobic bacterial growth; A: freshly prepared electrode; B: the same electrode, after a chronoamperometric experiment as in Fig. 1(a) for 2 h.

formance than the 2-fluoro compound. This result can mainly be interpreted by means of a considerable improvement of the tolerance of platinum against poisoning caused by a stronger interaction between platinum and fluorine substituted polyanilines. A catalytic effect of the polymer itself can most likely be excluded considering the quite positive redox potential of the fluorine substituted polymers (2FPA: 400 mV , TFPA: 475 mV).

Noteworthy, the electropolymerization of poly(tetrafluoroaniline) carried out at a potential of 1.6 V instead of 1.3 V results in an additionally increased

electrode performance. This improvement, however, cannot be attributed to an alteration of the voltammetric behaviour of the film, which remains mainly unaffected (not shown). In the case of poly(2-fluoroaniline) and polyaniline a higher deposition potential do not result in an increased catalytic activity. In contrary, unsubstituted polyaniline faces degradation caused by overoxidation followed by hydrolysis.

The electrode performance can be further improved by a simple in situ reactivation step which is applied regularly in order to inverse the poisoning once it took place. The reactivation can be achieved either by oxidative [1] or by reductive stripping. Thus, by shortly exposing the anode to a potential positive to the dashed line in Fig. 1(b) (curve A*) chemisorbed species are oxidatively removed from the electrode surface and electrode regains its full catalytic activity see (e.g. [20]). At electrodes modified with 2FPA and TPA the reactivation can also be achieved by simply opening the electrical circuit which due to the reductive conditions in the fermenting medium (the open circuit potential is approximately -600 mV) leads to the reductive stripping of the chemisorbed species from the electrode. This approach is preferable since it does not require energy to be put into the system. Fig. 2 demonstrates that the application of such reactivation procedure helps improving and maintaining catalytic activity of a fuel cell anode. The current traces, which possess a typical sawtooth like pattern, represent the performance of differently modified platinum electrodes (A–D) and, for comparison, of an unmodified graphite electrode (E). As expected, unmodified carbon does not respond to the

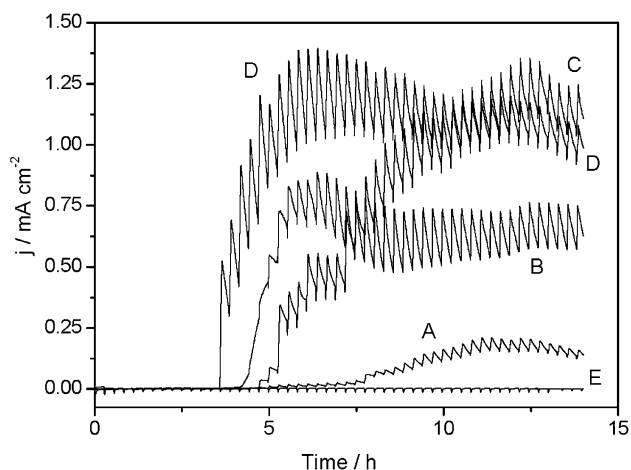


Fig. 2. Current generation of a freshly inoculated anaerobic culture of *E. coli* K12 in a standard glucose medium as in Fig. 1(a). In an interval of 1000 s potential pulses of 1 V were applied for 5 s in order to prevent the loss of electrode activity. During the potential pulsing the current recording was interrupted. A: unmodified platinum electrode; B: polyaniline modified Pt electrode; C: poly(2-fluoroaniline) modified Pt electrode; D: poly(tetrafluoroaniline) modified Pt electrode. E: unmodified carbon electrode.

fermentation processes. Also, bare platinum exhibits an unsatisfying performance (curve A). Similar to the results shown in Fig. 1(a), the poly(2-fluoroaniline) and poly(tetrafluoroaniline) modified platinum electrodes yield the highest current densities, the current density being increased by the factor of 2.5 compared with Fig. 1(a). An evaluation of the current densities at the differently modified electrodes with and without the application of a reactivation procedure is given in Table 1. Due to a considerably lower catalytic activity of polished platinum, used in the here presented experiments, in comparison to platinum black modified electrodes, which possess a greatly increased activity, the current densities shown here are somewhat lower than those reported previously [1].

Evidently, the suitability of a polymer modified electrode as an anode material for a microbial fuel cell greatly depends on its ability to resist microbial or chemical degradation. This is not a matter of discussion for microbially mild conditions, as for instance for the fermentation of glucose by *E. coli* K12. It becomes, however, crucial when the fuel cell anode is exposed to microbially aggressive conditions and complex microbial communities [21], as they are found for instance in sewage sludges. Here, the polymer itself might serve as a substrate for different kinds of bacteria to feed on [22]. Preliminary experiments conducted in sewage sludge samples confirm this assumption. They showed that, depending on the microbial and chemical composition of the sludge, polyaniline is often removed from the anode within a few hours and sometimes even minutes. This process leads to an immediate poisoning of the platinum and to a loss of its electrocatalytic activity. Other biocompatible redox polymers like poly(neutral red) were expected to share the fate of the polyaniline. Assuming the generally poor ability of microorganisms to metabolize fluorinated organic compounds the polyfluoroanilines and especially the perfluorinated polyaniline were expected to be resistive towards microbial

Table 1
Mean current densities at differently modified platinum electrodes

Electrode material	Current density ($\mu\text{A cm}^{-2}$)
Pt	11
Pt ^a	188
Pt/PANI	90
Pt/PANI ^a	850
Pt/2-FPA	454
Pt/2-FPA ^a	1310
Pt/TFPA	533
Pt/TFPA ^a	1350

The electrodes were placed in a stirred anaerobic culture of *E. coli* K12 in a standard glucose medium ($c_{\text{glucose}} = 0.55$ mmol L⁻¹). A potential of 0.2 V (vs. Ag/AgCl sat. KCL) was applied.

^a Electrode was subject of a regenerative potential pulsing in order to maintain its catalytic activity (in an interval of 1000 s potential pulses of 1 V, 5 s were applied).

decomposition. In fact, polytetrafluoroaniline was found to be fully resistant. Even after five days of storage in the sewage sludge the polymer layer remained intact. Also, the catalytic activity of the electrode was still unaffected. Poly(2-fluoroaniline), however, did not meet the expectation. Similar to polyaniline the stability of the polymer was insufficient. The high stability and performance of the polytetrafluoroaniline modified anode material was also confirmed in experiments with strains of the *Clostridia* family [23], known for their ability for reductive biotransformation [22].

4. Conclusions

With this contribution we demonstrate that fluorine-substituted polyanilines are highly useful for conductive polymer/electrocatalyst composite anode materials for microbial fuel cells. Compared to polyaniline and other conductive polymers the fluorine substituted polymers poly(2-fluoroaniline) and poly(2,3,5,6-tetrafluoroaniline) appear superior in their support of the catalytic activity of platinum. The excellent stability of the tetrafluorinated polyaniline against microbial degradation favours this polymer for application as electrode modifier in microbially aggressive environments like sewage or sewage sludge.

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