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ORIGINAL PAPER

Investigation of the electrocatalytic oxidation of formate and ethanol at platinum black under microbial fuel cell conditions

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Abstract In this communication, we discuss the electro-oxidation of the fermentation products formate and ethanol at platinum black modified electrodes under microbial fuel cell conditions, i.e., at neutral pH, room temperature, and in microbial culture solutions. The electrocatalytic oxidation was studied using cyclic voltammetry, chronoamperometry, and potentiostatic coulometry. Current densities up to 6 mA cm^{-2} at 0.2 V oxidation potential and 97% coulombic efficiency were observed for the electro-oxidation of 100 mM solutions of formate in pH 7 buffer solution. Electrode deactivation could be successfully prevented using an oxidative potential reactivation procedure. Polymer coating, however, fully stopped the formate oxidation. As expected, the electro-oxidation of ethanol was less efficient—with a limiting current density being 600 μA cm^{-2}.

Keywords Electrocatalysis · Platinum · Ethanol · Formate · Electro-oxidation · Microbial fuel cell

Introduction

The electrocatalytic oxidation of small inorganic and organic compounds, e.g., CO, alcohols, and volatile fatty acids at platinum catalysts has been widely investigated for acidic conditions [1–7]. Especially methanol and ethanol are of great interest, as they are favourable fuels for the combustion in fuel cells. The electro-oxidation of these organic compounds at platinum at low potentials, however, is negatively affected by the formation and strong adsorption of CO (and methane) species at the electrocatalyst. The mechanisms of this CO poisoning has been intensively studied by Lamy and coworkers [2, 7]. The electro-oxidation of formic acid is often considered as a simplified model for the oxidation of methanol. Kita et al. [8] proposed a reaction mechanism of formic acid electro-oxidation and the related poisoning processes at platinum electrodes. Great research efforts have been dedicated to the improvement of the electro-oxidation by using alloys of platinum with, e.g., tin, ruthenium, and rhenium, with nickel [9, 10] and also Pt composites with WO_3 [11]. The presence of these metals or their oxides in the electro-catalyst reduces the oxidation potential of CO and thus prevents the catalyst inactivation. Another possibility to increase the catalytic activity of platinum is to use Pt nanoparticles confined to molecular sieves based on silicate [12]. Chromium–phosphorus phases have been reported also to catalyze the methanol oxidation in acidic solutions [13].

Conventional fuel cells like direct methanol, ethanol, and formic acid fuel cells are generally operated at elevated temperature and either under strongly acidic or alkaline conditions [14, 15]. Our interest, however, is focused on the possibilities of facilitating the electrocatalytic oxidation of microbial metabolic products like hydrogen, volatile organic acids, and alcohols in microbial fuel cells—under the physiological conditions of the bacterial growth, i.e., at ambient temperature, pressure, and neutral pH.

In several studies, we have already demonstrated an efficient direct oxidation and depletion of microbial hydrogen, produced by heterotrophic and phototrophic microorganisms from different carbohydrate sources [16–

Dedicated to Professor Dr. Alan M. Bond on the occasion of this 60th birthday.

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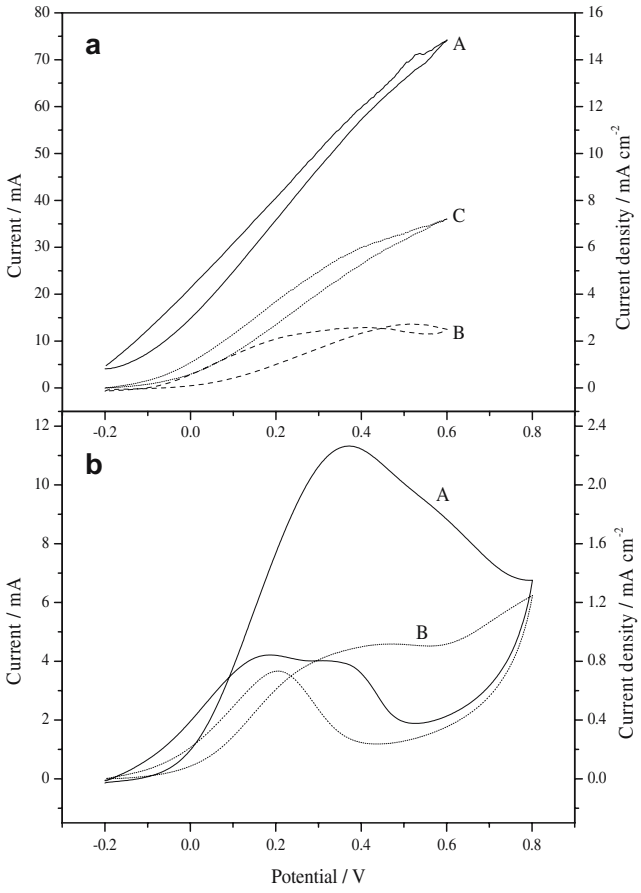

Fig. 1 Cyclic voltammograms of the electrocatalytic oxidation of **a** formate and **b** ethanol at platinum black modified platinum paddle electrodes (5 cm^2 projected surface area), measured in pH 7 phosphate buffer solution. The scan rate was 10 mV s^{-1}. The voltammograms were recorded before and after the exhaustive electrochemical oxidation, shown in Fig. 2. **a**-*A*: 91 mM sodium formate; **b**-*B* 14.6 mM formate (after 22 h of electrochemical oxidation at 0.2 V, experiment Fig. 2); **a**-*C*: After re-addition of sodium formate to a final concentration of 75 mM. **b**-*A*: 98 mM ethanol; **b**-*B*: 89 mM ethanol (after 17 h of electrochemical oxidation at 0.2 V, experiment Fig. 2)

19]. For that we have developed a novel sandwiched anode material [17, 19, 20] consisting of a noble metal electrocatalyst and a polymer overlay that prevents the electrocatalyst from poisoning. To increase the versatility and efficiency of such microbial fuel cell system, it is necessary to access as many electron-rich fermentation products as possible for direct oxidation and electricity generation. In this communication, we present the results of a study on the electrocatalytic oxidation of formate and ethanol, major products of different microbial fermentation pathways, at platinum black electrodes and polyaniline-modified-platinum electrodes under microbial fuel cell conditions. Experiments were performed in synthetic buffer solution and in anaerobic solutions of living cells *Escherichia coli* K12.

Materials and methods

Electrochemical instrumentation

All experiments were carried out using a conventional three-electrode arrangement. Silver–silver chloride electrodes, sat. KCl, 0.195 V vs SHE, served as reference electrodes. The counter electrodes were graphite rods. They were separated from the electrolyte solution by a Nafion 117 perflourinated membrane. The working electrodes, platinum paddle electrodes (geometrical active surface area 5 cm^2), were electrochemically platinized for 500 s at a potential of −0.6 V in a stirred acidic solution containing 12 mM H_2PtCl_6 (Fluka). For comparative studies, some electrodes were subsequently coated with polyaniline [19]. 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} H_2SO_4 and 0.1 mol l^{-1} aniline (scan rate 0.1 V s^{-1}, 15 cycles) [21]. All current density values in this communication refer to the geometrical electrode surface area.

All experiments were conducted using Autolab potentiostats (PSTAT10, PGSTAT20 and 30, Ecochemie, Netherlands). The PGSTAT 30 was equipped with five array modules allowing multi-working electrode measurements. Chronoamperometric measurements and potentiostatic coulometry were performed at 0.2 V, a potential typical for low external load conditions in microbial fuel cells [19]. Electrode inactivation, caused by the incomplete oxidation of the target substrates and other oxidizable compounds in the bacterial medium [19], was prevented by using in situ regenerative potential pulsing as it was presented in previous papers [19, 20]. For that, in intervals of 1,000 s, a potential of 1 V was applied for 5 s to the working electrode to oxidatively strip off chemisorbed species from the electrode surface. The pulse was followed by 5 s equilibration (open circuit).

Except for the experiments that were performed using anaerobic living cultures of *E. coli*, all electrochemical experiments were carried out in pH 7 phosphate buffer solutions (50 mM KH_2PO_4; 50 mM K_2HPO_4).

Substrate conversion analysis

Substrate exhaustion and product formation were followed by HPLC analysis. The HPLC (Knaur, Germany) 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 with 0.005 n sulfuric acid as the eluent; the detector was a differential refractometer.

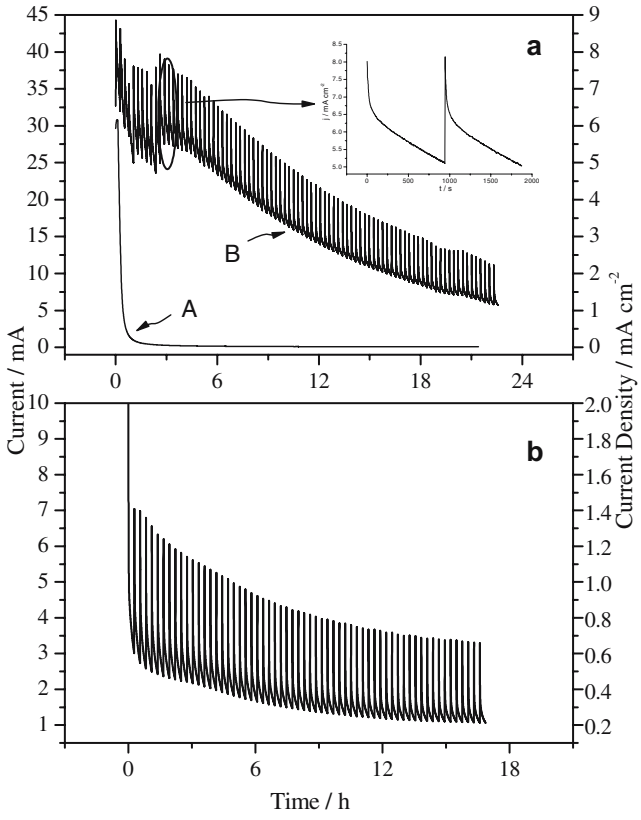

Fig. 2 Chronoamperograms recorded at platinum black electrodes (5 cm^2 geometrical surface area) immersed in 100 ml, pH 7 phosphate buffer solutions (stirred). **a** The solution contained 91 mM *formate* (initial concentration); *curve* (A): constant potential, without electrode regeneration protocol; *curve* (B): application of the oxidative regeneration procedure; **b** The electrolyte solution contained 98 mM *ethanol* (initial concentration). The experiment was performed using the regenerative potential pulsing

Bacterial growth

Escherichia coli K12 was kindly provided by the Division of Applied Microbiology, Institute of Microbiology and Molecular Biology, University of Greifswald. The aerobic cultivation and anaerobic electrochemical experiments were performed in standard growth medium containing 10 g glucose, 5 g yeast extract, 6.8 g potassium dihydrogen phosphate, and 8.7 g dipotassium hydrogen phosphate per liter. The pH was adjusted to 7 before autoclaving. The cultivation was carried out at 37 °C.

Results and discussion

Figure 1a-A and b-A show the cyclic voltammograms of the electrocatalytic oxidation of formate and ethanol at platinum black electrodes in pH 7 phosphate buffer solution, i.e., in the absence of microorganisms. The figures illustrate the high catalytic activity of platinum black towards formate and ethanol electro-oxidation under neutral pH conditions. The sufficiently low open-circuit potentials of around −0.2 V (vs Ag/AgCl) and current densities of 8 mA cm^{-2} (formate, 91 mM) and 1.5 mA cm^{-2} (ethanol, 98 mM) at 0.2 V are promising for a potential application in microbial fuel cell systems.

When conducted under constant potential (chronoamperometric) conditions, the electrocatalytic oxidation was accompanied by electrode inactivation effects. This deactivation—as demonstrated for the example of the formate oxidation in Fig. 2a, curve (A)—leads to a rapid decay of the current density of the formate oxidation to values under 0.2 mA cm^{-2} within 1 h of operation. The phenomenon is well-known and is mainly caused by the poisoning of platinum during the oxidation process [2, 8, 22].

As demonstrated before [19] and as shown in Fig. 2a, curve (B), such deactivation effects can be reversed and the electrode activity maintained by applying an oxidative in situ reactivation protocol (described in the Materials and methods section). By implementing such procedure, an average current density of 6 mA cm^{-2} was maintained for several hours before it slowly decreased to 1 mA cm^{-2} after 22 h due to substrate exhaustion (see HPLC data, Table 1).

Table 1 Comparison of the coulombic yield of oxidation of formate and ethanol with chemical analysis data

	Formate	Ethanol
Initial conc.[a]	91 mM	98 mM
End conc.[a]	14 mM	89 mM ethanol; 1.2 mM acetate; 6 mM acetaldehyde
Educt conversion	77 mM[b]	7.2 mM[c]/(9 mM)[b]
Theoretical coulombic yield[d]	1,486 C	162 C
Experimental coulombic yield[e]	1,431 C	121 C
Deviation of experimental yield from theoretical yield	−3.7%	−25.3%

Electrocatalytic oxidation was performed in synthetic phosphate buffer solution (absence of microorganisms)
[a] Determined via HPLC analysis
[b] Computed as the difference between the initial and end concentrations of the educt
[c] Calculated from the sum of oxidation products
[d] Calculated from the educt conversion (chemical analysis) using Faraday's law
[e] Determined by integration of chronoamperometric data as presented in Fig. 2

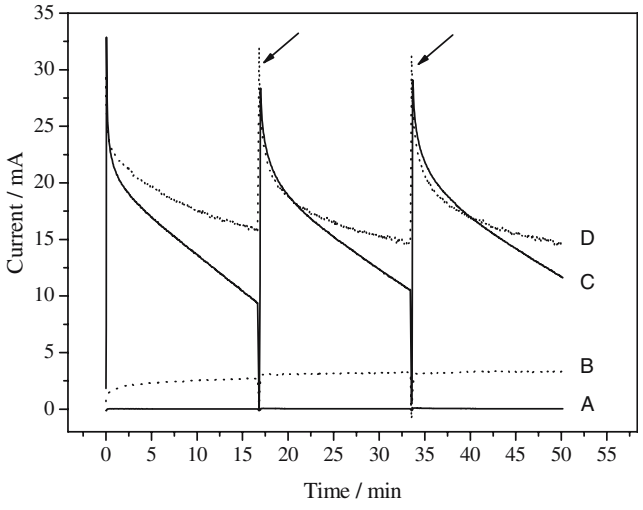

Fig. 3 Chronoamperometric experiment of the electrocatalytic oxidation of formate (100 mM) in 100 mM phosphate buffer solution, pH 7. (*A*) Polyaniline modified platinum black electrode (Pt-PANI) in formate solution; (*B*) Pt-PANI in hydrogen saturated formate solution; (*C*) platinum black electrode in formate solution; (*D*) Pt black electrode in hydrogen saturated formate solution. The potential of the electrodes was 0.2 V. The *arrows* indicate the application of the regenerative oxidative potential pulsing procedure (1 V, 5 s; the current recording was paused during the pulsing)

The decrease of the formate concentration by 85% during the experiment shows that formate was efficiently electro-oxidized. As shown in Table 1, the electrochemical conversion of formate is almost identical with the conversion found by chemical analysis (deviation of 3.7% only). Cyclic voltammograms, recorded after the potentiostatic experiment, confirm that the current decrease is mainly caused by substrate exhaustion (Fig. 1a-B and a-C). Re-addition of substrate—in this case, to a final concentration of 75 mM formate—doubled the current density (I-C). Nevertheless, the lower current density, compared to the initial values, indicates that irreversible poisoning effects also play some role. The most probable explanation for the beneficial role of the oxidative pulsing is the oxidative stripping of blocking compounds from the electrode surface. However, it cannot be excluded that the cyclic polarisation also leads to surface reconstructions resulting in keeping the real electrode surface area of the active platinum large. This will be the subject of further studies.

As expected, the electro-oxidation of ethanol was considerably less efficient than the formate oxidation. At low potentials, the oxidation usually ends at the state of acetaldehyde, the further oxidation to acetate usually requires higher oxidation potentials or the supporting effect of alloy metals, such as ruthenium or tin [7]. At the beginning of the experiments, average current densities of about 700 μA cm^{-2} were achieved. As in the case of formate oxidation, an electrode deactivation was observed, which could partly be overcome by using the described oxidative potential pulsing procedure (Fig. 2b). However, after 17 h of potentiostatic electrolyses, the current density decreased to 250 μA cm^{-2}, although about 91% of the substrate was still present in the electrolyte solution (Table 1). As shown in the cyclic voltammograms in Fig. 1(b-B), the current decrease goes along with a decrease of the electrocatalytic activity of the Pt black electrode.

In Table 1, the data of the coulometric and molar analysis of the experiments are provided. They show that the products of the ethanol oxidation, determined by HPLC, are mainly acetaldehyde (6 mM) and acetate (1.2 mM). A comparison of the theoretical and the experimental recovery rate (162 C and 121 C, respectively) reveals a deviation of about 25%. This deviation is to be ascribed to the contribution of the oxidative electrode regeneration procedure to the substrate oxidation: Only during the regeneration steps (1 V, 5 s, every 1,000 s) adsorbed ethanol is oxidized to acetate, at 0.2 V the oxidation terminates at the stage of acetaldehyde. Calculating the expected charge from the amount of acetaldehyde formed during the electrolyses supports this assumption, as the calculated 116 C are in good agreement with the experimental results.

An interesting finding of this study was that the extent of ethanol oxidation could not be enhanced by increasing the mass transport via stirring. This result is indicative of the particularly slow oxidation of the adsorbed ethanol at bare platinum under our experimental conditions.

As we have shown before, the poisoning of platinum electrocatalysts, used as anode material for direct hydrogen oxidation in microbial fuel cells, is significantly decreased when the electrode is covered by a layer of a conductive polymer (polyaniline or its derivates [20]). Most likely, this protection 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 [23–25]. To compare polyaniline modified platinum (Pt-PANI) with unmodified platinum, both electrodes were tested towards their electrocatalytic activity for formate oxidation in the absence as well as in the presence of hydrogen in the solution. The results are presented in Fig. 3. A number of quite remarkable details can be derived from this figure. The first observation is the fact that formate oxidation at Pt-PANI is not possible.

In Fig. 3, curve (A), it appears that the polymer layer physically blocks the organic substrate from approaching the electrocatalyst. The unmodified platinum black electrode shows the typical saw-tooth like shape of the current–time curve, caused by the regular reactivation of the electrode. When hydrogen is bubbled through the formate solution, the additional depolarizer leads to an almost equal increase of the current at both Pt and Pt-PANI electrodes (curves B and D), showing that both electrodes possess a similar electrocatalytic activity towards hydrogen oxidation.

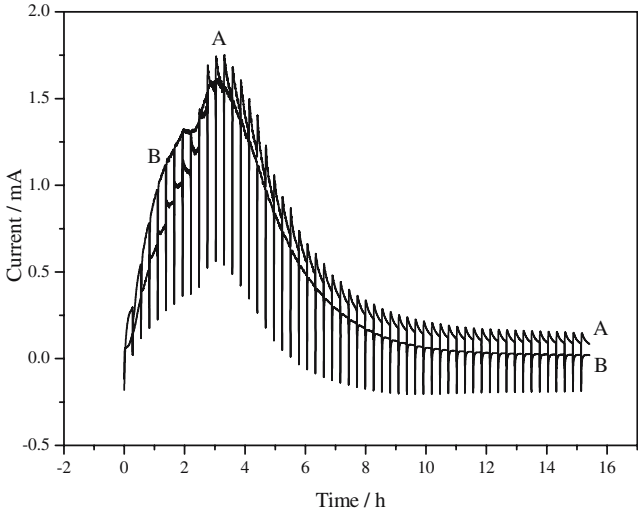

Fig. 4 Comparative chronoamperometric measurement recorded in a freshly inoculated anaerobic *Escherichia coli* culture at 37 °C. E_{WE}=0.2 V. Two working electrodes (platinum paddle electrodes of 5 cm^2 geometrical surface) were measured simultaneously: *A*—platinum black modified; *B*—platinum black modified, covered by conducting polymer polyaniline. The experiment was conducted in 100 ml stirred bacterial medium, using the regenerative potential pulsing procedure

In the case of Pt-PANI, however, the electrode did not show any sign of deactivation during the experiment. It becomes obvious that one major electrode protection mechanism of the polyaniline coating is the physical blocking of molecules from the electrode surface due to their size, or charge, whereas a dissolved gas like hydrogen can easily penetrate and reach the electrocatalyst.

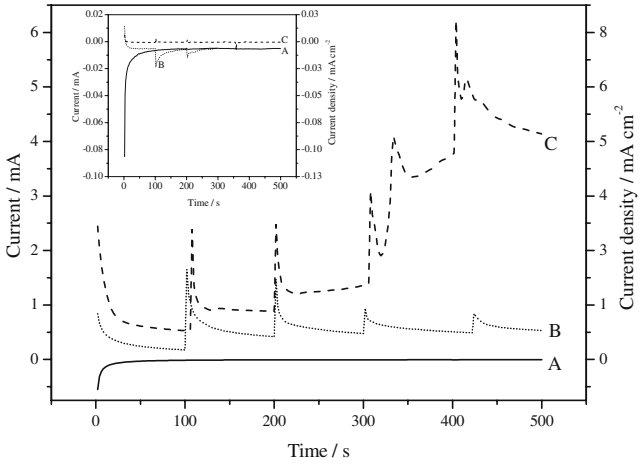

Fig. 5 *Main figure*: Chronoamperometric measurements performed at 0.2 V in 100 ml 100 mM phosphate buffer (pH 7) under stepwise reagent addition. *A*: nitrogen gas purged solution. *B*: incremental addition of ethanol (5 ml, 100 mM ethanol every 100 s). *C*: incremental addition of sodium formate (5 ml, 100 mM every 100 s). *Inset figure:* Experiment as above, but in 0.1 M H_2SO_4. *A*: nitrogen purging; *B*: incremental addition of ethanol, and *C*: sodium formate addition. The working electrodes were platinized platinum wire electrodes (0.787 cm^2 geometrical surface)

To combine an efficient formate and hydrogen oxidation we performed initial experiments using Pt-PANI-Pt modified electrodes, i.e., polyaniline modified platinum electrodes that were subsequently modified with platinum nanoparticles in or on the PANI film. These electrodes indeed showed promising electrocatalytic properties. Further studies, however, are required to optimize the electrode modification, in particular with respect to a minimisation of the platinum load.

Figure 4 shows the result of a chronoamperometric measurement conducted in a freshly inoculated *Escherichia coli K12* medium. Electrode A was a platinum black modified electrode; electrode B was Pt-PANI. The bacterial medium contained glucose as the substrate, which was converted by the microorganisms via the mixed acid fermentation path, and under anaerobic conditions, into electron- and energy-rich metabolic products like hydrogen, formate, ethanol, acetate and succinate. As we have shown before, it is possible to efficiently oxidize the microbial hydrogen directly in the microbial medium by using Pt-PANI (or Pt-poly(tetrafluoroaniline)). As shown in Fig. 3, however, Pt-PANI is not capable of oxidizing the organic fermentation products. The current response of this electrode has consequently to be attributed exclusively to hydrogen oxidation. Using unmodified platinum the additional oxidation of organic fermentation products should be possible - provided that a reactivation procedure is applied to maintain the electrode activity.

At the beginning of the experiment, during the log-phase of the bacterial growth, both electrodes show similar activities, Pt-PANI (to be recognized by its smoother chronoamperogram) showing slightly better performance. At this point, the concentrations of organic fermentation products are still low and in the slow build-up.

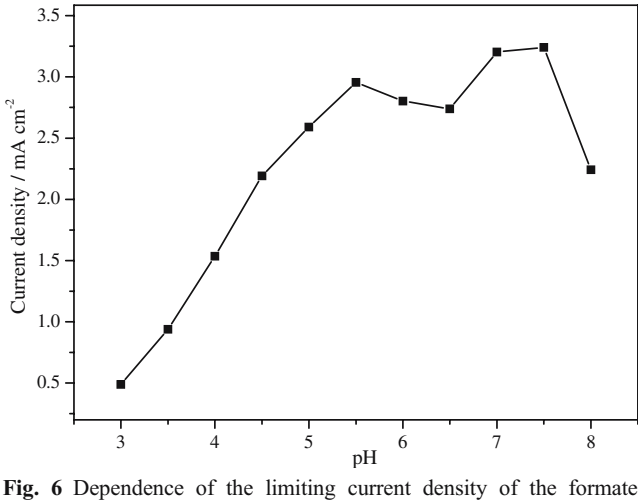

Fig. 6 Dependence of the limiting current density of the formate oxidation at platinum black modified platinum electrodes on the solution pH. (E_{WE}=0.2 V, 100 mM phosphate buffer solution containing 100 mM sodium formate)

With progressing experiment, when the microbial hydrogen production decreases and the concentrations of the organic fermentation products have built up (usually 5 to 20 mM of formate and ethanol are formed), the current density of the Pt electrode grows over that of Pt-PANI. The current of the latter electrode decreases to approach zero after approximately 12 h due to substrate exhaustion and finished fermentation. The Pt black electrode, however, still continued delivering oxidation current due to the present level of dissolved formate and ethanol.

As depicted in the chronoamperometric curves in Fig. 5, the oxidation of formate and ethanol at the platinum black modified electrodes is strongly pH-dependent. The chronoamperograms show the current response when incremental amounts of substrate are added to a pH 7 phosphate buffer solution (main figure) or to 0.1 M sulphuric acid. Curve A shows the background current, curves B and C the current responses when ethanol and formate were incrementally added to reach the final concentration of 20 mM after the fifth addition. For the phosphate buffer solution current densities of about 5 mA cm^{-2} (formate) and 0.5 mA cm^{-2} (ethanol) were obtained.

The inset of Fig. 5 shows the results of an experiment equal to that in the main figure but conducted in 0.1 M sulphuric acid. It is interesting to find that under the acidic conditions, both ethanol and formate oxidation do not appear to proceed to a significant extent. Whereas the ethanol addition did not significantly change the background current (which is slightly negative: −7 μA cm^{-2}) the addition of formate resulted in only a small increase of the current signal.

In Fig. 6, the dependence of the current density of the formate oxidation on the solution pH is illustrated. The presented data represent the limiting current densities determined in potentiostatic experiments at the respective pH values. The figure clearly supports the above observation—the current density of the formate oxidation grows as the solution pH increases. It reaches its maximum between pH 5.5 and 7.5. From the viewpoint of microbial fuel cells, this result is very important and promising, as that pH range is optimal for microbial growth.

Conclusion

Formate and ethanol are major products of microbial fermentation processes. With this basic study we have demonstrated that it is possible to utilize these metabolic products of microbial cultures, provided electrocatalytic platinum black electrodes are utilized in conjunction with a regenerative electrode pulsing. The rate of the electrocatalytic formate oxidation was found to be significantly higher (tenfold) than that of ethanol. The current density for the ethanol oxidation may appear low; however, it is comparable to values reached in recent types of microbial fuel cells. The pH range of optimum microbial activity, i.e., pH 5 to 7, was found most suitable for the electro-oxidation processes.

In previous communications, we have shown that hydrogen gas produced in microbial cultures under anaerobic conditions can be effectively oxidized by polyaniline and poly(tetra-fluoraniline)-covered platinum electrodes. The present paper clearly shows how it may be possible to tailor electrodes in such way that the goal of microbial fuel cells is realized, i.e., the complete, or almost complete, electrochemical oxidation of all the metabolic products of anaerobic cultures. At the very end of these developments, the microbial cultures will be used only to digest complex organic materials, e.g., cellulose, lignin, etc., to produce small metabolites as electron carriers that can be oxidized on electrodes.

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