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Effects of substrate and metabolite crossover on the cathodic oxygen reduction reaction in microbial fuel cells: Platinum vs. iron(II) phthalocyanine based electrodes

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ABSTRACT

Crossover processes between anode and cathode compartment are important factors that limit the efficiency and performance of fuel cells. This applies not only to chemical but also to biological fuel cells like microbial fuel cells. Whereas effects of an oxygen crossover from the cathode to the anode compartment of microbial fuel cells have already been qualitatively described, the effects of a crossover of organic matter from the anode compartment to the cathode have not yet been studied. In this communication the influence of typical MFC substrates and metabolites on the cathodic oxygen reduction reaction (ORR) at platinum and at pyrolysed iron(II) phthalocyanine (pyr-FePc) based electrodes is studied. It is demonstrated that the performance of platinum is substantially diminished in the presence of these compounds, whereas the ORR performance at pyr-FePc remains largely unaffected. The presence of sulphide, however, inhibited the electrocatalysis at both materials.

1. Introduction

Common to the great majority of fuel cells is the use of oxygen as the cathode oxidant [1]. Despite the many advantages of this omnipresent oxidant, a comparably slow kinetics of the oxygen reduction reaction, ORR, represents a severe performance bottleneck especially in low temperature fuel cells [2]. Benchmark ORR electrocatalyst for low temperature fuel cells is platinum, though its high price has triggered an intensive search for alternative catalyst materials. A further weakness of platinum as ORR catalyst is based on its actual strength – its versatility to serve as oxidation as well as reduction catalyst. Thus, the permeation of fuel from the anode through the separator membrane into the cathode compartment (fuel crossover) leads to the formation of mixed potentials and the flow of internal currents – causing a depolarization of the electrode even at open circuit [3]. A well-studied example for such crossover effects is the methanol crossover in direct methanol fuel cells that leads to the depolarization of the Pt based cathodes (see, e.g. [4]).

A major group of potential alternative electrocatalysts is based on metal porphyrines and phthalocyanines (e.g. iron(II) phthalocyanine (FePc)) [5] and related transition metal complexes [6,7]. These biomimetic materials have been shown to be remarkably insensitive against the crossover of methanol (see, e.g. [8,9]) which makes them, despite of their lower ORR performance, to interesting alternatives to platinum.

Recently, we have shown that in microbial fuel cells the specific operation conditions (e.g. the low ionic strength and buffer capacity and the almost neutral pH of the electrolyte solution) cause further strong limitations on the oxygen reduction reaction [10]. Additionally, as in chemical fuel cells, crossover processes like the oxygen flow into the anode compartment as well as substrate diffusion to the cathode take place [11]. Naturally, these crossover effects are most pronounced in separator free designs.

So far, alternative MFC cathode catalysts were studied exclusively from the pure performance point of view, crossover effects not being explicitly addressed. In this communication we compare the ORR activity of platinum and pyrolysed iron(II) phthalocyanine (pyr-FePc) in the presence of typical microbial substrates and metabolites. The effects of the organic materials on the limiting oxygen reduction current densities are studied and the formation of mixed potentials is discussed. Further, the influence of catalyst poisons like sulphide on both catalysts is studied.

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2. Experimental

2.1. Chemicals

All chemicals (p.a.) were obtained from Sigma–Aldrich, Germany.

2.2. Catalyst preparation

Pyr-FePc was prepared from a mixture of 50 wt% iron(II) phthalocyanine and Vulcan XC-72 (Cabot Corp.) via pyrolysis as described in Ref. [12]. The platinum catalyst (C1-20, 20 wt% Pt on Vulcan XC-72, E-Tek, BASF, Germany) was used as purchased.

2.3. Electrode preparation

The cathode backbone material was graphite foil (Chempur©, Karlsruhe, Germany), 1 cm^2 active surface area. The electrocatalyst was mixed manually with 20 μL of a 30 wt% poly(tetrafluoroethylene)/water dispersion; 3 mg of the mixture were transferred onto the graphite foil and was allowed to dry at room temperature overnight, or at least 3 h.

2.4. Electrochemical characterization

All electrochemical experiments were performed using a PGSTAT 30 potentiostat/galvanostat (EcoChemie, Netherlands). The reference electrode was a Ag/AgCl sat. KCl (Sensortechnik Meinsberg, Germany). A rotating electrode module 616 EG&G was used with the foil electrode clamped in a self-made electrode holder vertically and axially symmetrically. The rotation rate was 1000 rpm. The galvanodynamic experiments were performed at a scan rate of 10^{-7} A s^{-1}. All experiments were performed with a 1 h equilibration time prior to the experiment; the electrolyte solution was continuously purged either with N_2 or with air.

The effect of microbial substrates and metabolites on the cathode performance was studied in a concentration range between 1 and 10 mM. This concentration range reflects different conditions in microbial fuel cell MFC – low concentrations referring to low crossover in membrane separated systems, high concentrations reflecting the conditions in membrane-less systems. The nature of the chosen substrates and metabolites as well as the chosen concentrations is exemplary and may differ in actual bioelectrochemical systems.

All experiments were performed in 100 mM, pH 7 phosphate buffer solution.

3. Results and discussion

Fig. 1 shows exemplary Tafel plots of the electrocatalytic oxygen reduction reaction at platinum and pyr-FePc at neutral pH in the absence (**A**, **B**) and in the presence (**A**′, **B**′) of 5 mM formate. Fig. 1 is plotted with two *x*-axes. Whereas the lower *x*-axis provides the electrode potential with respect to the reference electrode potential, the upper *x*-axis shows the overpotential of the electrode for the oxygen reduction reaction $\eta_{O_2/H_2O} = E^{\Theta'}_{O_2/H_2O} - E_{\text{electrode}}$. Here $E^{\Theta'}_{O_2/H_2O}$ represents the standard ORR potential, calculated for an air saturated phosphate buffer solution (~8.4 mg L^{-1} [13]) at 22 °C to be 762 mV vs. NHE (equal to 565 mV vs. Ag/AgCl). It is clearly visible that even in 100 mM “pure” phosphate buffer, the platinum electrode (curve **A**) does not reach the theoretical ORR potential. This deviation has to be attributed to minute impurities in the electrolyte solutions [3], as well as to the slow kinetics at the ORR at platinum near the standard oxygen reduction potential [2]. An even considerably stronger deviation of the open circuit potential is observed for the pyr-FePc cathode (curve **B**). Here, the lower reduction potential is mainly attributed to the incomplete oxygen reduction (partial production of H_2O_2) at this electrode material [14]. A comparison of platinum and pyr-FePc under such clean electrolyte conditions would undoubtedly lead to a preference for platinum as cathode catalyst. Yet, as already emphasized in the introduction, the practical working environment of MFC cathodes involves the presence of organic substrates and microbial metabolites, which may severely affect the cathode performance. Therefore, Fig. 1, curve **A**′, depicts the polarization behaviour of platinum in the same electrolyte solution as for curve **A**, but containing 5 mM of formate, a typical microbial fermentation product. As it is clearly visible, the presence of this low concentration of formate considerably (by 163 mV) lowers the open circuit potential of the platinum cathode and thus the open circuit voltage of a resulting MFC. Quite different is the result for the pyr-FePc electrode. As the Tafel plot of this electrode (Fig. 1, **B**′) depicts, the open circuit potential and the polarization behaviour of this electrode material in the formate containing electrolyte solution is practically identical to the pure electrolyte solution (curve **B**).

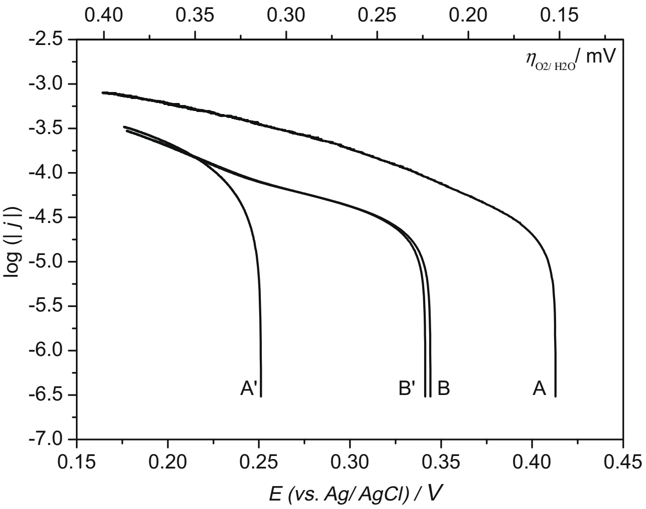

Fig. 1. Tafel plots of **A** a platinum and **B** a pyr-FePc catalyst electrode in air purged, 100 mM, pH 7 phosphate buffer solution. The plots **A**′ and **B**′ show the ORR performance of the same electrodes after addition of 5 mmol L^{-1} Na-formate to the electrolyte solution.

In the presence of formate, platinum reaches the performance of pyr-FePc only at overpotentials larger than 350 mV (see Fig. 1, curves **A**′ and **B**′), under mass transfer limitation. Under these conditions, however, an increase of the electrode loading of FePc [10] and an improved catalyst manufacturing [15] may allow a considerable increase of the ORR performance of the FePc based electrode at considerably lower costs than in the case of platinum.

Fig. 2 schematically summarizes the effects derived from Fig. 1. When formate reaches a platinum cathode, it can be directly oxidized, thus providing electrons for the oxygen reduction reaction at the same catalyst moiety (Fig. 2A). This reaction can be interpreted as an internal short circuit reaction [16]. As Fig. 2A shows, this internal short circuit results in the formation of a mixed potential that lies between the redox potential of oxygen and that of formate, thus significantly lowering the open circuit potential of the cathode. As shown in Table 1, the extent of the potential shift is strongly dependent on the formate concentration. At increasing formate concentration (here at 10 mM) the potential even shifts to negative values. Now, the formate oxidation over-compensates the oxygen reduction and j_{0V} becomes positive, which means that an oxidation net current instead of a reductive current flows.