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ELECTROOXIDATION OF NEAT HIGHER ALCOHOLS CATALYSED BY COBALT PORPHYRIN

ELEKTROUTLENIANIE CZYSTYCH WYŻSZYCH ALKOHOLI KATALIZOWANE PORFIRYNĄ KOBALTOWĄ

Abstract

Waste alcohols might become excellent sources of energy in its higher forms like electric energy provided suitable catalysts could be found for their electrooxidation. Cobalt porphyrin appeared to be active in this process. Alcohols are oxidised in their neat forms at potentials of porphyrin ring oxidation, which might indicate that the reaction proceeds not on the metal centre but rather by activation of carbon electrode. The reaction is kinetically sluggish. Cobalt porphyrin was found active in the oxidation of ethylene glycol and glycerol in DMF at potentials even lower than those on bulk platinum but at a lower current.

Keywords: direct alcohol fuel cell, electrooxidation of alcohols, cobalt tetraphenylporphyrin

Streszczenie

Odpadowe alkohole mogą się stać doskonałymi źródłami energii w jej wyższej postaci, jak energia elektryczna, pod warunkiem, że znajdują się katalizatory ich elektROUTLENIANIA. Porfiryne kobaltowa okazała się aktywną w tym procesie. Alkohole ulegały utlenieniu w ich czystych postaciach przy potencjałach utleniania pierścienia porfiryne, co mogłoby wskazywać, że reakcja zachodzi raczej nie na metalu, ale przez aktywację elektrody węglowej. Reakcja jest kinetycznie powolna. Stwierdzono, że porfiryne kobaltowa jest aktywna w utlenianiu glikolu etylenowego i glicerolu w DMF przy potencjałach nawet niższych, niż te dla litej platyny, ale z mniejszym prądem.

Słowa kluczowe: bezpośrednie alkoholowe ogniwo paliwowe, elektROUTLENIANIE alkoholi, tetra-fenylporfiryne kobaltowa

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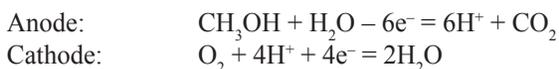
1. Introduction

Is it not wasteful to use energy resources inefficiently? And how else could be considered just burning the fuel, be it even waste fuel, to produce merely thermal energy. It can be converted, admittedly, to more useful, higher forms of energy, like electric energy or energy of light, but a part of it must dissipate as required by the second law of thermodynamics. In direct generation of electric energy, like it occurs in direct fuel cells, this principle must also be obeyed but less energy is lost due to practical reasons. For a process to proceed with high efficiency it must approach reversibility. For a heat engine it means operating at the maximum flame temperature with oxygen supplied, generally beyond 3000 K, with all the final product dissociation reactions excluded, which is impossible. Fuel cells operate at room or elevated temperatures, generally below the fuel boiling point. Thus there is no concern over the dissociation of the final products, process temperatures do not pose any problems to materials and much less heat is lost with exhaust gas [1]. These are the reasons for much higher energy efficiencies of fuel cells, reaching in practice 70%, compared with maximum 46% for steam turbines or a world record of 52% for the largest diesel engine in the world, and even with the record breaking 60% efficiency of a combined GE power plant. The efficiency of thermal engines is generally associated with their size, the larger they are the higher the efficiency, while fuel cells may be used even in relatively small vehicles or portable consumer electronic devices, which makes them even more useful.

There has been a wide interest in methanol fuel cells, including direct cells [2], that use methanol specifically produced for this purpose. Ethanol easily obtained from fermentation processes has also gained interest [3], despite problems with its inefficient oxidation. Typically, acetate is the main final product and less than 5% is converted to carbonates [4]. On the other hand, mixtures of higher alcohols, ethylene glycol (spent antifreeze or break fluid) [5] or glycerol [6] as waste from biodiesel manufacturing that could also be effectively used for electric energy generation receive much less interest. They are often burnt, which may be not that efficient if they are mixed with water. In such cases they might even be processed in wastewater treatment plants, which means that all the energy possible to get from them will be dissipated. From all those alcohols and mixtures of them energy may be produced provided they are used in direct fuel cells. Table 1 below summarises the standard enthalpy and Gibbs free energy values for the full combustion of the alcohols along with the theoretical energy efficiency calculated as the ratio of ΔG° to ΔH° , and the maximum attainable voltage of the fuel cell.

Values calculated are based on standard molar enthalpies of formation, standard molar Gibbs free energies of formation and standard molar entropies [7]. Cell voltage was calculated from $\Delta_c G^\circ$ value.

As can be seen from the Table, alcohols may be efficient sources of electric energy. The electrode reactions are as follows:



Here they are given for methanol. The potential of respective half-cells will be a function of pH value. This affects the potential of both half-cells in opposite directions and thus not of the

entire cell, hence it will not be discussed. It can also be seen that for the anodic reaction a source of oxygen is needed, in this case it was a molecule of water.

Table 1

Standard enthalpy and Gibbs free energy of full combustion of liquid neat selected alcohols (to liquid water and carbon dioxide gas), maximum voltage of the direct fuel cell and theoretical maximum energy efficiency at 298 K and 100 kPa

Alcohol	$\Delta_c H/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_c G/\text{kJ}\cdot\text{mol}^{-1}$	E/V	$\eta/\%$
Methanol	-726.0	-702.0	1.21	96.7%
Ethanol	-1366.9	-1325.3	1.14	97.0%
Ethylene glycol	-1184.5	-1172.9	1.22	99.0%
1-Propanol	-2021.3	-1962.8	1.13	97.1%
2-Propanol	-2005.8	-1951.1	1.12	97.3%
Glycerol	-1654.3	-1653.2	1.22	99.9%
1-Butanol	-2675.9	-2600.7	1.12	97.2%
1-Pentanol	-3330.9	-3239.9	1.12	97.3%
1-Hexanol	-3984.4	-3876.5	1.12	97.3%

The critical parameter for the electrode reaction to proceed reversibly is the rate of the electrode processes, hence a catalyst is needed. Platinum and its alloys, particularly with ruthenium are by far the most popular [8], but they are too expensive to be used for waste materials. New active catalysts are to be sought for. Cobalt porphyrins are effective catalysts of oxidation processes [9]. On the one hand they are able to activate oxygen, on the other, they readily form hydride complexes (a similarity to platinum). They are also known to efficiently catalyse processes with hydrogen transfer, like hydrogen evolution [10, 11]. It should be mentioned that cobalt hydroxide was used as a co-catalyst on platinum for anodic oxidation of polyhydric alcohols [12].

Our studies have revealed that cobalt tetraphenylporphyrin (CoTPP) catalyses both the electrooxidation and electroreduction of neat alcohols. Electrooxidation of neat alcohols cannot lead to total oxidation of these compounds as there is not enough oxygen in the molecule. But the products of this reaction after winning some amount of energy can be further processed.

2. Experimental

Cyclic voltammetry measurements were done using a BAS 100B/W Electrochemical Workstation with a C3 Cell Stand (Bioanalytical Systems) with a standard three-electrode cell. The working electrode was a 1.6 mm diameter glassy carbon electrode (Mineral) and platinum wire was the auxiliary electrode. Typically, GCE was used in experiments, but 1.6 mm diameter bulk Pt disk electrode (Mineral) was also employed to compare catalytic activities. All potential were measured and quoted against an Ag/AgCl (3 M aqueous NaCl) electrode that was put into a double bridge filled in the upper part with 3 M aqueous NaCl

solution and in the lower part with supporting electrolyte solution, a cotton wool plug was placed between both solutions, and they were separated from the test solution by a dense ceramic frit. 0.1 M tetra-*n*-butylammonium tetrafluoroborate (Fluka) was employed as the supporting electrolyte solution. The ready solution was additionally dried with 4A molecular sieves. All measurements were done under dry argon atmosphere (Ar-N 5.0, Linde). Voltammograms were registered at 100 mV s^{-1} scan rate unless otherwise noted.

3. Results and discussion

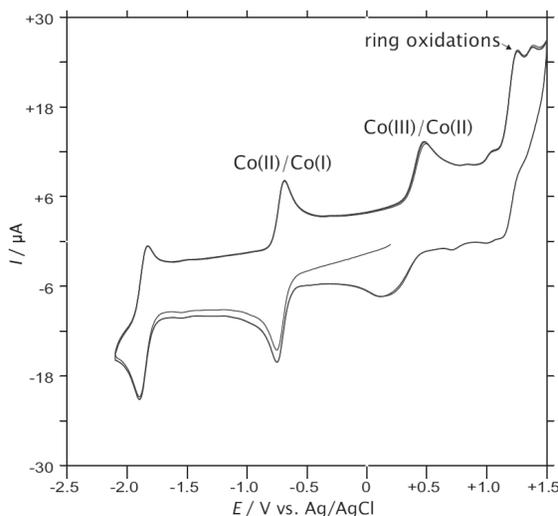


Fig. 1. Cyclic voltammogram of cobalt tetraphenyl porphyrin in dimethylformamide

Rys. 1. Woltamperogram cykliczny tetrafenylporfiryny kobaltowej w dimetyloformamidzie

Cyclic voltammogram of cobalt tetraphenyl porphyrin in solvents like dimethylformamide (Fig. 1) shows several processes. Their assignment is known from literature [13]. In alcohols it looks differently. Generally the Co(II)/Co(I) reduction is reversible, as in DMF, but at more cathodic potentials, alcohols are reduced. In the region between 0 and 0.5 V waves appear that may be ascribed to Co(II)/Co(III) oxidation. The next oxidation process, which usually appears at about 0.8 V, is much more intensive in alcohols. Its shape on the forward scan (Fig. 2), and in some cases on the reverse scan (Fig. 3), indicates that the process is accompanied by the oxidation of alcohol, which being the solvent, does not indicate current limitation due to diffusion.

The oxidation potential of butanol and pentanol is comparable to oxidation potential of methanol on platinum electrodes, which makes cobalt porphyrins interesting candidates for practical use. As can be seen in Fig. 4, for 1-hexanol, even an activation effect was observed, analogous to that on platinum for methanol oxidation [14]. In the case of platinum this unusual effect of rising anodic current on the reverse scan is explained by reduction of platinum oxide that blocks the electrode and inhibits methanol oxidation.

The current intensity of cobalt porphyrin catalysis is not satisfactory. As demonstrated in Figs. 5 and 6 by deconvoluted voltammograms recorded with various scan rates, it is due to the kinetics of the electrode process. Processes recorded with low scan rates show comparatively high currents. Comparing the intensity of one electron reduction Co(II)/Co(I) at ca. -1 V with those at $+0.8$ V, rough turnover numbers can be estimated. At higher scan rates there might be even no catalytic effect at all.

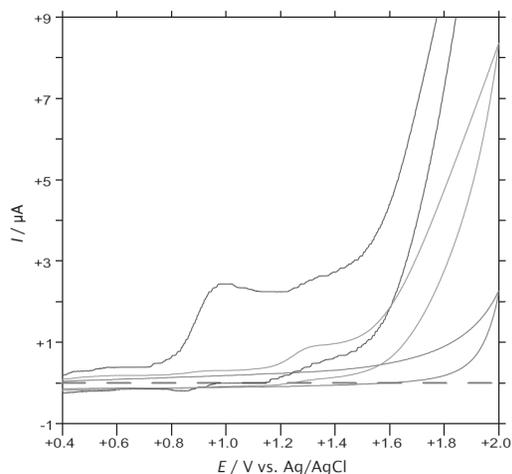


Fig. 2. 1-Butanol oxidation without and after addition of 1 mM and 3 mM CoTPP

Rys. 2. Utlenianie 1-butanolu bez i po dodaniu 1 mM i 3 mM CoTPP

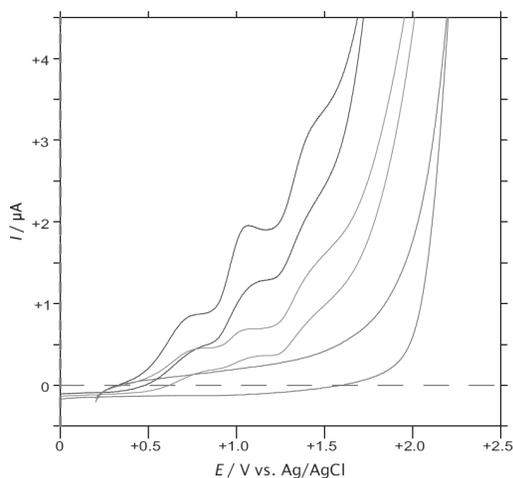


Fig. 3. 1-Pentanol oxidation without and after addition of 1.5 mM and 5 mM of cobalt tetrakis (4-bromotetrafenyl)porphyrin

Rys. 3. Utlenianie 1-pentanolu bez i po dodaniu 1,5 mM i 5 mM tetrakis (4-bromotetrafenylo) porfirynty

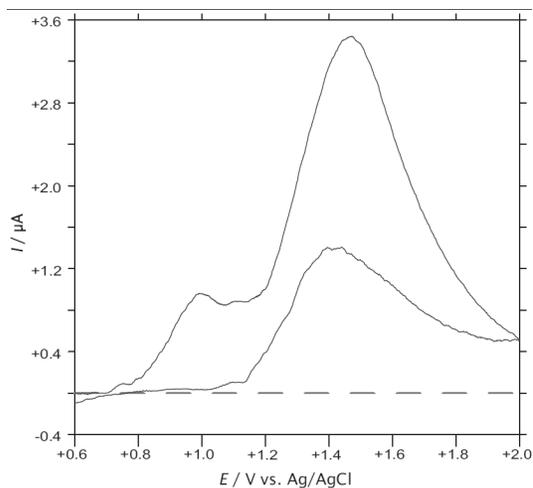


Fig. 4. 1-Hexanol oxidation after addition of 1.0 mM CoTPP with background subtracted showing an interesting activation effect on the reverse scan, similar to that observed in the oxidation of methanol on platinum

Rys. 4. Utlenianie 1-heksanolu po dodaniu 1,0 mM CoTPP po odjęciu tła wykazujące interesujący efekt aktywacji na skanie powrotnym, podobny do obserwowanego w utlenianiu metanolu na platynie

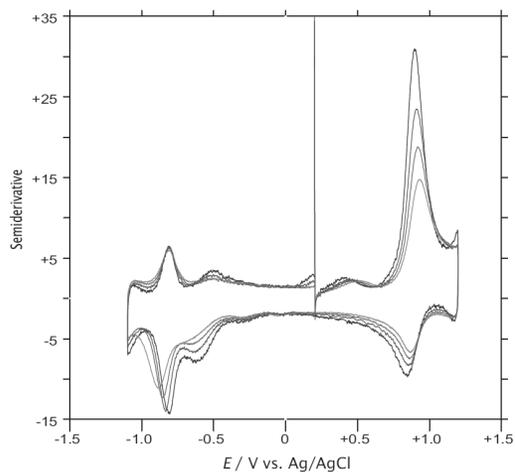


Fig. 5. Deconvoluted voltammograms of 1-butanol with 5 mM CoTPP added. Deconvolution removes the effect of diffusion and hence enables to directly compare the intensity of waves. Reduction at -0.8 V is one-electron Co(II)/Co(I) process. Scan rates used from $20 \text{ mV}\cdot\text{s}^{-1}$ (the most intense) to 200 (the least intense)

Rys. 5. Voltamperogram 1-butanolu z dodanym 5 mM CoTPP po dekonwolucji. Dekonwolucja usuwa efekt dyfuzji, a zatem umożliwia bezpośrednie porównanie natężenia fal. Redukcja przy $-0,8$ V jest jednoelektrodowym procesem Co(II)/Co(I) . Szybkości skanowania stosowane to od $20 \text{ mV}\cdot\text{s}^{-1}$ (sygnał największy) do $200 \text{ mV}\cdot\text{s}^{-1}$ (sygnał najmniej intensywny)

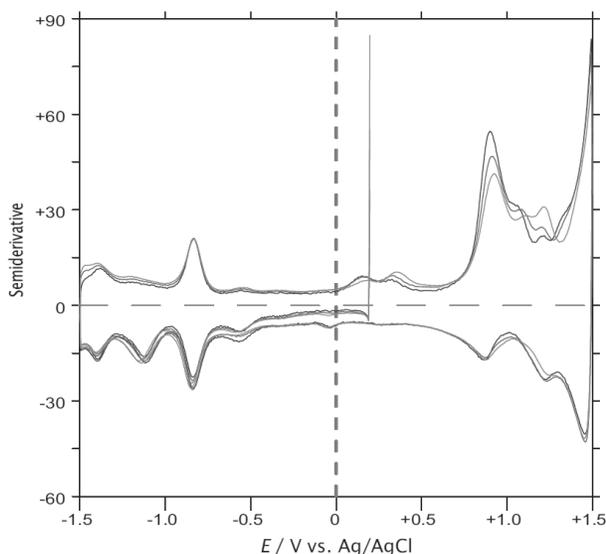


Fig. 6. Deconvoluted cyclic voltammograms of CoTPP in neat 1-pentanol. Shown are cyclic voltammograms recorded at 0.05, 0.10 and 0.20 V s^{-1} scan rates. The intensity of alcohol oxidation wave rises with decreasing scan rate

Rys. 6. Woltamperogramy cykliczne CoTPP w czystym 1-pentanolu po dekonwolucji. Pokazano woltamperogramy zarejestrowane przy szybkościach skanowania 0,05, 0,10 and 0,20 V s^{-1} . Natężenie fal utleniania alkoholu wzrasta ze zmniejszającą się szybkością skanowania

Curiously enough, the oxidation of alcohols occurs at the potential of ring oxidation, which might indicate that the catalytic centre might not be metal itself. It cannot be excluded that cobalt porphyrin activates somehow the carbon electrode. Such effects are known even in porphyrin chemistry. The famous NO detector electrode originally obtained from a nickel porphyrin on carbon fibre [15] shows activity after removing nickel [16].

As mentioned in Introduction, waste ethylene glycol and glycerol may be used for gaining energy but there are no efficient methods known to convert them to higher forms of energy. Cobalt porphyrin was tested for catalytic activity in electrooxidation of these polyhydric alcohols. This time it was not possible to add CoTPP directly into neat alcohols because it was not soluble in these systems. That is why it was decided to use DMF solutions instead.

As platinum is known for its catalytic activity in anodic oxidation of alcohols, its effect was compared with the effect produced by CoTPP in the oxidation of ethylene glycol, which is shown in Fig. 7. It should be mentioned, however, that bulk platinum, as in Pt electrode we used, is not the most active form of this metal because it shows significant poisoning effect. It appeared that currents are much higher on platinum, but the process occurs at much lower potentials on cobalt porphyrin. The wave exhibits two maxima, as if two hydroxyl groups were oxidised at two different potentials. a similar effect is observed for glycerol, also in DMF solution, as shown in Fig. 8. This time three peaks appear, as if confirming the hypothesis of hydroxyl groups being oxidised sequentially. In both cases, as already noticed for neat alcohols, oxidation proceeds at potentials of porphyrin ring oxidation.

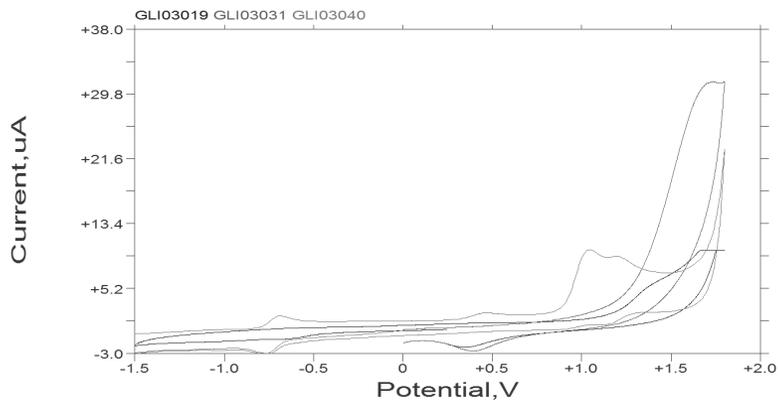


Fig. 7. Comparison of catalytic activity of bulk platinum and CoTPP in electrooxidation of ethylene glycol in DMF

Rys. 7. Porównanie aktywności katalitycznej litej platyny i CoTPP w elektrotlenianiu glikolu etylenowego w DMF

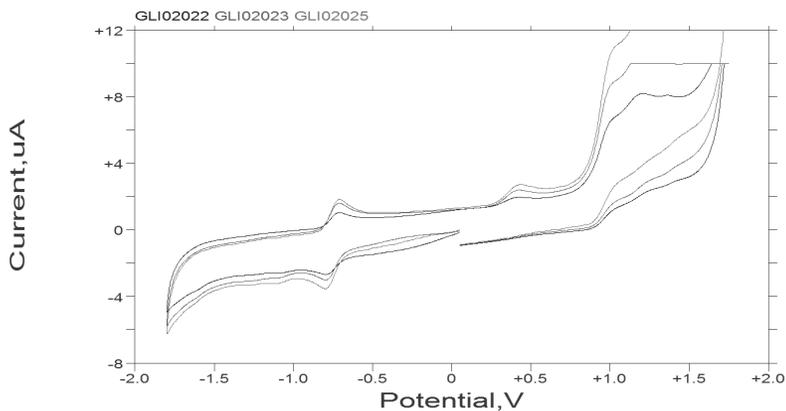


Fig. 8. Catalytic activity of CoTPP in electrooxidation of glycerol in DMF

Rys. 8. Aktywność katalityczna CoTPP w elektrotlenianiu glicerolu w DMF

4. Conclusions

Cobalt tetraphenylporphyrin catalyses the oxidation of neat alcohols (1-butanol, 1-pentanol, 1-hexanol) at potentials comparable to those of platinum catalysis of methanol oxidation.

In some cases, like 1-hexanol oxidation, activation phenomena are observed on the reverse scan, similar to those of platinum catalysed alcohol oxidation.

The catalysis is rather slow, deconvoluted voltammograms indicate sluggish kinetics of the electrode process.

CoTPP appeared to be active in electrocatalysis of ethylene glycol and glycerol in DMF. It gave lower currents than bulk platinum electrode, but oxidation occurred at much lower potentials compared to bulk platinum.

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