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Oxidation of formic acid on bulk and nanosized Pt-Co alloys

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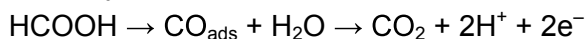
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Introduction

Organic liquids such as methanol and formic acid are considered as potential fuels in polymer electrolyte membrane fuel cell (PEMFC). Advantage of HCOOH over CH₃OH is its lower crossover through Nafion[®] membrane. Also, HCOOH is somewhat less toxic than CH₃OH. It is generally accepted that HCOOH oxidizes to CO₂ via a dual path mechanism [1]. Direct path is dehydrogenation of HCOOH molecule without the formation of CO:



A reactive intermediate in this reaction is likely to be formate species, HCOO [2]. Indirect path comprises dehydration of HCOOH with the formation of CO_{ads} and its further oxidation to CO₂:



At low potentials CO_{ads} can not be oxidized on Pt and it acts as the catalyst poison. Since low potentials are crucial for high performance of direct formic acid fuel cell (DFAFC), the presence of CO_{ads} on the anode surface is to be avoided or at least greatly reduced. This can be achieved by combining Pt with some other metal performing its role through (i) bifunctional mechanism, (ii) electronic effect, or (iii) ensemble or third-body effect. Bifunctional mechanism is operative when the second metal is capable to adsorb oxygen-containing species at lower potentials than Pt, so that CO_{ads} formed through HCOOH dehydration on Pt sites is oxidized by oxygen-containing species on the other metal sites. Electronic effect refers to the modification of the electronic structure of Pt atoms, generally resulting in change of the adsorption ability of Pt. If this modification weakens the bond between Pt and CO_{ads}, the electronic effect reduces Pt poisoning. The ensemble or third-body effect is based on the fact that the dehydration path requires at least three contiguous Pt atoms, whereas the dehydrogenation path requires at most two Pt atoms [3,4]. Therefore, when large Pt surface is interrupted by foreign atoms, dehydration path is favored and CO_{ads} formation is suppressed.

HCOOH oxidation has not been studied on Pt modified by 3 *d* transition metals. In our opinion, these systems deserve attention because 3 *d* transition metals possess two characteristics that can be beneficial for Pt activity. They are oxidized at lower potential than Pt, meaning that HCOOH oxidation can occur through bifunctional mechanism. Also, the electronic modification of Pt by 3 *d* transition metals due to both ligand [5] and strain [6] effect produces lowering of 3 *d* band center of Pt. This reduces electron back-donation from Pt to the adsorbates, such as CO, and weakens the bond between them. In this work we present the results of the HCOOH oxidation on bulk and nanosized Pt-Co alloys. These catalysts exhibited higher activity for oxygen reduction than Pt, which was ascribed to the inhibition of Pt-OH_{ads} formation on Pt sites electronically modified by Co atoms and surrounded by "oxide" covered Co atoms [7,8]. Besides, adsorption/desorption measurements of gaseous CO on Pt-Co alloy showed that CO binds more weakly to the Pt sites of the alloy than to pure Pt [9]. Therefore, we postulated that, along with the ensemble effect, which is purely geometric and should be exhibited by any foreign atom, Co can promote HCOOH oxidation through the bifunctional mechanism and the electronic effect.

Experimental

Polycrystalline Pt and thermally prepared Pt₃Co alloy electrodes in the form of disc were used in this study. Bulk composition of the alloy, assessed via X-ray fluorescence spectroscopy, was c.a. 75 at % Co. X-ray diffraction showed the specimen to be single-phase *fcc* solid solution of having the expected lattice constant for 75% Pt [7].

Nanosized electrocatalysts were commercial Pt, Pt₃Co and PtCo (20 mass% of total metal) supported on Vulcan XC-72 carbon black, provided by E-TEK. The catalysts were applied onto Au substrate in the form a thin layer. Catalyst powder was suspended in high purity water in the concentration of 2 mg cm⁻³. In all cases, 50 μl of the Nafion[®] solution (5 wt. %, 1100 E.W., Aldrich) was added per 1.0 cm³

of the suspension. After agitation in an ultrasonic bath, 10 μl of the suspension was placed onto Au electrode by micro-pipette and left to dry overnight.

A conventional electrochemical cell with a Pt counter electrode and a saturated calomel electrode (SCE) as the reference electrode was used. All the potentials reported in the paper are expressed vs. reversible hydrogen electrode (RHE). The supporting electrolyte of 0.1 M HClO_4 (99.999 % purity) was prepared with high purity water (Millipore). The electrolyte was deaerated by the bubbling the N_2 . Electrochemical oxidation of HCOOH was investigated in deaerated supporting electrolyte containing 0.5 M HCOOH . In the positive going scan, the potential was held at 0.10 V and HCOOH was added into the electrolyte. After 2 min the scan was continued at the rate of 1 mV s^{-1} (quasi steady-state measurements) or at 50 mV s^{-1} (potentiodynamic measurements). For the CO-stripping measurements, pure CO was bubbled through the electrolyte for 20 and 30 min while keeping the electrode potential at 0.10 V [10]. After purging the electrolyte by N_2 to eliminate the dissolved CO, the adsorbed CO was oxidized in an anodic scan at 20 mV s^{-1} . Two subsequent voltammograms were also recorded to verify the completeness of the CO oxidation. Real surface area of the Pt the Pt-Co electrodes were determined by the CO stripping method, assuming $420 \mu\text{C cm}^{-2}$ for the CO monolayer. The experiments were conducted at $298 \pm 0.5 \text{ K}$.

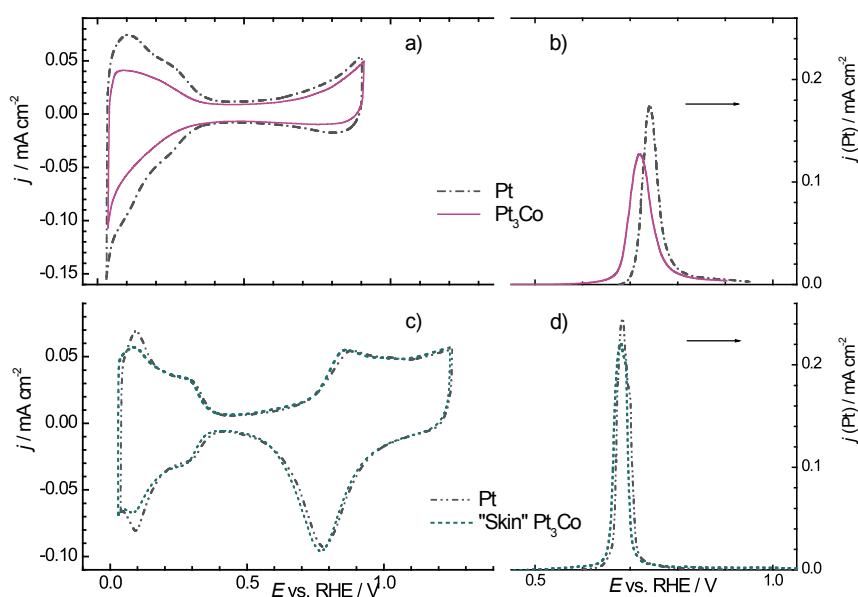


Fig. 1. Cyclic voltammograms of Pt_3Co bulk alloy and Pt electrode in the different potential ranges a) and c) (50 mV s^{-1}); b) and c) corresponding CO stripping voltammograms in 0.10 M HClO_4

Results and discussion

Cyclic voltammograms of Pt_3Co bulk alloy in 0.1 M HClO_4 solution are given in Fig.1 a) and c). When the potential was cycled up to 0.9 V (Fig.1a) a profile with weak features of hydrogen adsorption/desorption was obtained. No anodic dissolution of Co was observed within this potential window. Upon the extension of the positive potential limit, anodic current of Pt-oxide formation and possibly Co dissolution arose and the peaks for H adsorption/desorption on Pt gradually developed. Steady-state voltammogram of Pt_3Co alloy in the extended potential window corresponds to the voltammogram of bulk Pt (Fig.1c), except that the peaks at $\sim 0.1 \text{ V}$ in the H adsorption/desorption region are lower. These peaks are assigned to the weakly adsorbed H. Nevertheless, Co is likely to be completely leached from the surface of the alloy, so this Pt_3Co surface can be held as the "skin structure" [7].

The stripping voltammograms of CO_{ads} were recorded on Pt, Pt_3Co and the "skin" Pt_3Co surface and the results are given in Fig.1 b) and d). Stripping of preadsorbed CO was used for the Pt surface area determination, and this experiment also gives insight in the kinetics of CO oxidation, which is a possible reaction step in HCOOH oxidation. The charge for Pt_3Co alloy, cycled up to the potential region 0.90 V, is lower and the corresponding CO stripping voltammogram is shifted to less positive potential than for Pt electrode. That indicates existence of the electronic effect in the alloy and weaker bond of the CO and Pt atoms in presence of Co atoms, as it was expected [5,6]. As one can see, the onset potential and the peak potential, as well as the charge under the peaks for Pt and the "skin"

Pt₃Co surfaces are approximately the same, indicating that Co is leached from the surface and that roughness factor of the surface is not enlarged during the formation of the skin structure. Polarization curves for the HCOOH oxidation were recorded at Pt₃Co alloy and compared to those on Pt and Pt-skin structure. From potentiodynamic profiles and quasi steady-state curves,

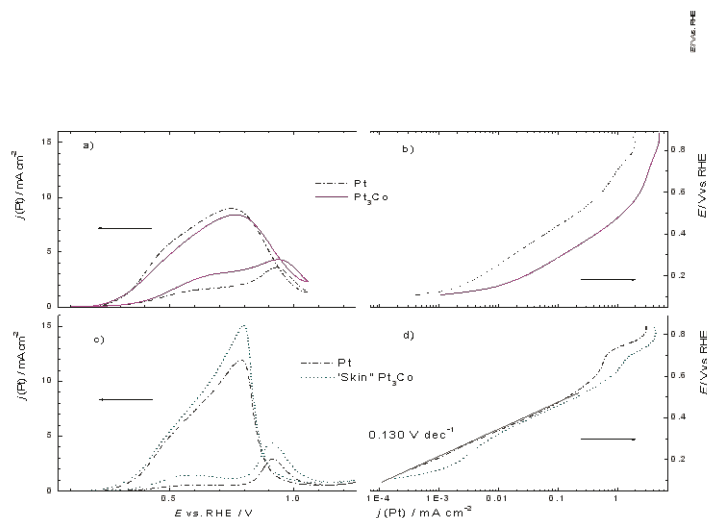


Fig.2. Potentiodynamic polarization curves (a and c) and quasi steady-state curves for the oxidation of HCOOH.

presented as the Tafel plots (Fig.2), it can be seen that the onset potential is slightly less positive for Pt₃Co alloy than for the other two electrodes. The current densities at Pt₃Co and Pt-skin electrode are higher than at pure Pt. However, all potentiodynamic curves recorded in the forward direction display the plateau and the peak at ~0.9 V and much higher current densities in the backward sweep. In addition, Tafel slopes are from 130 to 150 mV dec⁻¹, which also implies high surface coverage by CO_{ads} [11,12]. The enhancement factor of Pt₃Co alloy versus pure Pt is about seven.

Steady-state cyclic voltammograms of Pt₃Co/C, PtCo/C and Pt/C catalysts, corresponding oxidation of preadsorbed CO and HCOOH oxidation curves in 0.1 M HClO₄ are presented in Fig. 3. As on bulk Pt and Pt-Co alloy, H adsorption/desorption peaks are well-resolved on Pt/C, but not at the alloy catalysts. Formation of Pt-oxide on Pt₃Co/C and PtCo/C catalysts is delayed with respect to Pt/C. As seen, the oxidation of CO_{ads} starts earlier on the Pt-Co than on pure Pt nanoparticles. This result and the delayed formation of Pt-oxide on the Pt-Co alloy particles suggest that the bonds between CO and OH species and Pt atoms in alloys are weaker than in the case of Pt atoms in the pure Pt particles.

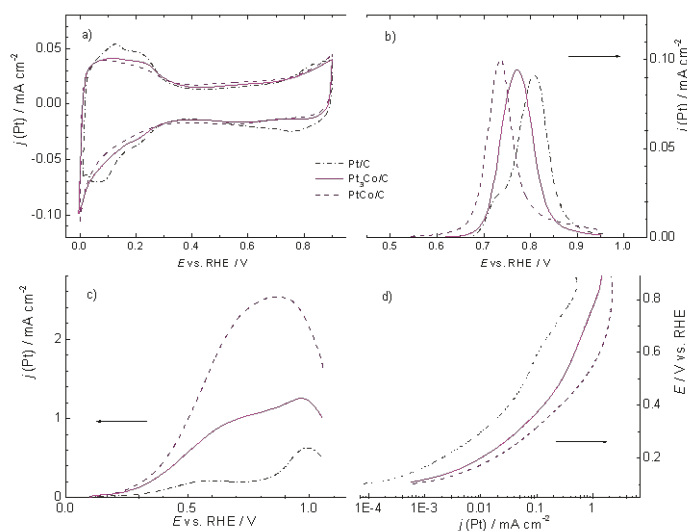


Fig. 3. a) Cyclic voltammograms of nanocatalyst; b) corresponding CO stripping voltammograms; c) and d) anodic potentiodynamic polarization curves and quasi steady-state curves for the HCOOH oxidation.

In the Pt/C catalyst we used in the experiments the Pt particles are 2.5 ± 0.2 nm in diameter [13], while Pt-Co particles are larger - the diameters of Pt₃Co and PtCo particles are 3.4 ± 0.7 nm and 4.4 ± 0.7 nm, respectively [7]. The position of the CO_{ads} stripping peaks, as seen in Fig. 3b, follows the same order as the particle size being more positive for the smaller particles. Moreover, the CO_{ads} stripping on bulk Pt electrode cycled in the same potential range exhibits the lower peak potential, which confirms the particle size effect in the adsorption on Pt surfaces. This effect can be explained by the different d-band center of low and high coordinated atoms. The first ones, which are more abundant on the surfaces of small particles, have narrower d-band because of lower degree of overlapping between the atomic orbitals. The narrowing of the d-band increases the energy of the d-band center and, consequently, leads to stronger bond with the adsorbates.

Potentiodynamic polarization and quasi steady-state curves of HCOOH oxidation, presented in the form of Tafel plots, on Pt₃Co/C and PtCo/C catalysts are compared to Pt/C in Fig.3c and Fig.3d, respectively. The curve for Pt/C is characteristic for the electrode blocked by CO_{ads}, because of the current increase at ~ 0.8 V due to the oxidative removal of CO_{ads} by the adsorbed OH. According to this, surface poisoning by CO_{ads} is reduced in the presence of Co in the catalyst, especially in the case of PtCo/C. When PtCo/C was subjected to the prolonged potential cycling in order to leach Co from the surface of the nanoparticles, the polarization curve of HCOOH oxidation gained the same shape as for Pt/C. This experiment shows that Co atoms beneath Pt surface have no effect on Pt electrochemical activity, i.e. that a moderate promotion of the HCOOH reaction rate on Pt-Co surfaces originates predominantly in the ensemble effect. This explains why PtCo/C is more active than Pt₃Co/C – fraction of Co on the Pt₃Co surface is too low to produce significant ensemble effect.

Conclusion

The results of H and CO adsorption on Pt and Pt₃Co bulk alloys indicate weak electronic effect of Co on Pt. This effect could not be confirmed on the nanoparticles because of the strong influence of the particle size and the surface structure on the adsorption processes. Bimetallic Pt-Co surfaces express moderate promotion of the HCOOH oxidation kinetics with respect to pure Pt, which is mostly ascribed to the ensemble effect. However, the fraction of Pt on the bimetallic surfaces was too high at the all catalysts examined for the complete suppression of the indirect path in HCOOH oxidation, so CO_{ads} was produced on the electrode surface. Since weakening of Pt-CO_{ads} bond by the presence of Co was not significant, the poisonous CO_{ads} could not be efficiently removed and the enhancement factor in HCOOH oxidation of only seven was achieved for PtCo/C vs. Pt/C catalyst.

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