

Short communication

# Carbon supported Pt–Co (3:1) alloy as improved cathode electrocatalyst for direct ethanol fuel cells

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## Abstract

In direct alcohol fuel cells, ethanol crossover causes a less serious effect compared to that of methanol because of both its smaller permeability through the Nafion<sup>®</sup> membrane and its slower electrochemical oxidation kinetics on a Pt/C cathode. The main interest in direct ethanol fuel cells (DEFCs) is to find an anode catalyst with high activity for the oxidation of ethanol. However, due to the low activity of pure platinum for the oxygen reduction reaction (ORR), research on cathode electrocatalysts with improved ORR and the same or improved ethanol tolerance than that of Pt are also in progress. In this work, a commercial carbon supported Pt–Co (3:1) electrocatalyst (E-TEK) was investigated as cathode material in DEFCs and the activity compared to that of Pt. In the cathodic potential region (0.7–0.9 V versus RHE) Pt/C and Pt–Co/C showed the same activity for the oxidation of crossover ethanol. But the performance of Pt–Co/C as cathode material in DEFCs in the temperature range 60–100 °C is better than that of Pt/C both in terms of mass activity and specific activity, due to an improved activity of the alloy for oxygen reduction. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Ethanol; Fuel cell; Cathode; Pt–Co/C; Electrocatalysts

## 1. Introduction

The advantages of fuel cells as clean and silent power sources have been demonstrated, and the proton exchange membrane fuel cell (PEMFC) is presently one of the most promising devices [1,2]. The use of methanol as energy carrier and its electrochemical oxidation in direct methanol fuel cells (DMFCs) represents an important challenge for the polymer electrolyte fuel cell technology, because the complete system would be simpler without a reformer. However, methanol has some disadvantages, e.g. it is relatively toxic, inflammable with a low boiling point (65 °C), and it is not a primary fuel, neither a renewable fuel. Therefore, other alcohols, like ethanol, are being considered as alternative fuels. Ethanol is the major renewable biofuel and is less toxic than methanol. Wang et al. [3] compared the performance of fuel cells operating on various alcohols and found that ethanol is a promising alternative fuel with an electrochemical activity comparable to that of methanol.

Platinum is at present the best-known catalyst for the dissociative adsorption of small organic molecules. However, its activity for the oxidation of ethanol is low and it is not very effective to break the C–C bond. Recent studies indicate that binary quasi non-alloyed Pt–Sn catalysts [4,5] promote the oxidation of ethanol at lower potentials than on pure platinum.

In direct ethanol fuel cells (DEFCs), the ethanol fed to the anode compartment can permeate through the electrolyte to the cathode, similar to the case of the direct methanol fuel cell. Song et al. [6] found that the effect of ethanol permeated to the cathode is less serious than that of methanol because of both its smaller permeability through Nafion<sup>®</sup> and its slower oxidation kinetics on the Pt/C cathode. However, research on alternative cathode catalysts is still necessary in order to find a material with an improved ORR activity and a higher ethanol tolerance than those of Pt.

PMFCs fuelled with hydrogen showed improved performances when Pt–Co/C alloy catalysts were used as cathode materials instead of Pt/C [7–10]. The enhancement in the ORR activity observed for supported Pt–Co alloy electrocatalysts was ascribed to both geometric (decrease of the Pt–Pt bond distance) and electronic (increase of Pt d-electron vacancy) factors [5,11].

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Particularly, an improved performance in PEMFCs when using E-TEK Pt–Co/C (3:1) as cathode material, instead of Pt/C, was observed by Mukerjee and Srinivasan [12]. So, in this short communication the ethanol tolerance of a commercial carbon supported Pt–Co electrocatalyst (E-TEK) in the nominal Pt:Co atomic ratio 3:1 was evaluated and compared to that of Pt, through tests in a DEFC carried out at various temperatures. Kinetic analysis carried out in  $0.1 \text{ mol L}^{-1} \text{ HClO}_4$  revealed an ORR activity enhancement (per Pt surface atom) of ca. 1.5 for the E-TEK Pt–Co/C (3:1) electrocatalyst in comparison with Pt/C [13].

## 2. Experimental

X-ray diffractograms were obtained in a universal diffractometer Carl Zeiss-Jena, URD-6, operating with Cu K $\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) generated at 40 kV and 20 mA. Scans were done at  $3^\circ \text{ min}^{-1}$  for  $2\theta$  values between  $20^\circ$  and  $100^\circ$ .

To carry out tests in a single DEFC fed with ethanol/oxygen, the electrocatalysts were used to make two layer gas diffusion electrodes (GDE). A diffusion layer was made with carbon powder (Vulcan XC-72) and 15 wt.% (w/w) PTFE and applied over a carbon cloth (PWB-3, Stackpole). On top of this layer, the electrocatalyst was applied in the form of a homogeneous dispersion with Nafion<sup>®</sup> solution (5 wt.%, Aldrich) and isopropanol (Merck). All electrodes were made to contain  $1 \text{ mg Pt cm}^{-2}$ .

The oxidation of ethanol on Pt–Co/C and Pt/C was tested by linear sweep voltammetry in a single cell configuration fed with a  $1.0 \text{ mol L}^{-1}$  ethanol solution. The potential range was 0.1–0.9 V versus RHE and the experiments were done at 60 and  $90^\circ \text{C}$  with a 1285 A Solartron Potentiostat, using the software CorrWare for Windows (Scribner). The cell was purged with hydrogen at the cathode and with nitrogen at the anode side. In this way, the cathode serves as reference and counter electrode and the anode acts as the working electrode.

For the DEFC studies, the electrodes were hot pressed on both sides of a Nafion<sup>®</sup> 115 membrane at  $125^\circ \text{C}$  and  $50 \text{ kg cm}^{-2}$  for 2 min. The Nafion<sup>®</sup> membranes were pre-treated with a 3 wt.% solution of  $\text{H}_2\text{O}_2$ , washed and then treated with a  $0.5 \text{ mol L}^{-1}$  solution of  $\text{H}_2\text{SO}_4$ . The geometric area of the electrodes was  $4.6 \text{ cm}^2$ , and the cathode material was 20 wt.% Pt/C. The cell polarization data at 60, 80, 90 and  $100^\circ \text{C}$  and 3 atm  $\text{O}_2$  pressure were obtained by circulating a  $1 \text{ mol L}^{-1}$  aqueous ethanol solution at the anode.

## 3. Results and discussion

The XRD patterns of the carbon-supported Pt and Pt–Co (3:1) catalysts are shown in Fig. 1, and the corresponding crystallographic parameters are summarized in Table 1. The diffraction peak at  $20\text{--}25^\circ$  is attributed to the (002) plane of the hexagonal structure of Vulcan XC-72 carbon. The XRD patterns clearly show the five main characteristic peaks of the face-centred cubic (fcc) structure of crystalline Pt, namely, the planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2). The shift to higher angles of the Pt peaks in the Pt–Co electrocatalyst reveals alloy formation between Pt and Co, due to the incorporation of the base metal into

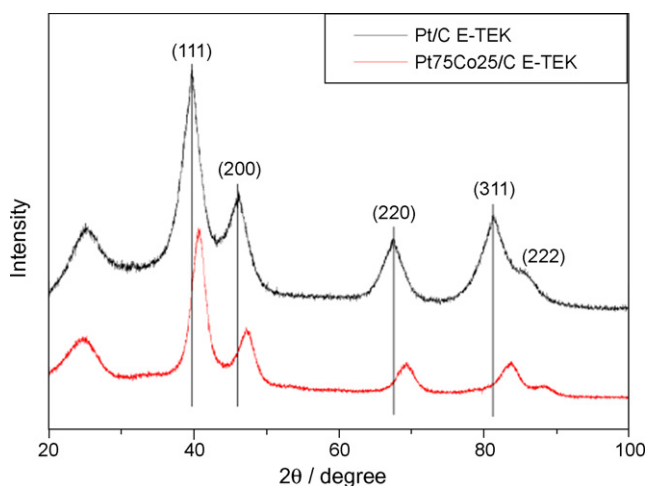


Fig. 1. XRD patterns of E-TEK carbon supported Pt and Pt–Co electrocatalysts.

the fcc structure of Pt. No superlattice reflexions were present in the XRD pattern of Pt–Co, which indicates the formation of only a disordered solid solution. No peaks for pure Co or its oxides were observed, but their presence cannot be discarded because they may be present in a small amount or even in an amorphous form. The lattice parameter of the Pt–Co/C (3:1) alloy electrocatalyst is in agreement with the lattice constant for the bulk Pt–Co (3:1) solid solution (0.383 nm [14]), indicating a high degree of alloying. Thus, it can be concluded that either there are no metal oxide species in this material or the amount is very small. The average size of the Pt and Pt–Co crystallites was estimated from the XRD (220) peak by using Scherrer's equation [15] and the values are shown in Table 1.

Fig. 2 shows the linear sweep voltammograms for ethanol oxidation at 60 (Fig. 2a) and  $90^\circ \text{C}$  (Fig. 2b) on Pt–Co/C (3:1) and Pt/C catalysts by E-TEK. For fuel cell applications, the working potentials of interest for the cathode are located between 0.7 and 0.9 V versus RHE. The onset potential of Pt–Co/C is slightly lower than that of Pt/C, but in the cathodic potential region the activity of both materials for ethanol oxidation is nearly the same.

From a practical point of view, the single cell test is the ultimate evaluation criterion for electrocatalyst materials. Also, the working conditions such as temperature, pressure, fuel flows, etc. are crucial to determine the performance of a fuel cell system. Therefore, being the cathode catalyst the only variable element in this study, the differences in single cell performances with different cathode catalysts are a consequence of the different activities of the cathode catalysts. The DEFC polarization curves for Pt–Co/C (3:1) and Pt/C by E-TEK at

Table 1  
Crystallographic parameters and roughness factors of E-TEK Pt–Co/C and Pt/C electrocatalysts

Catalyst	Lattice parameter (nm)	Crystallite size (nm)	Roughness factor
Pt–Co/C	0.383	2.8	1002
Pt/C	0.391	3.5	902

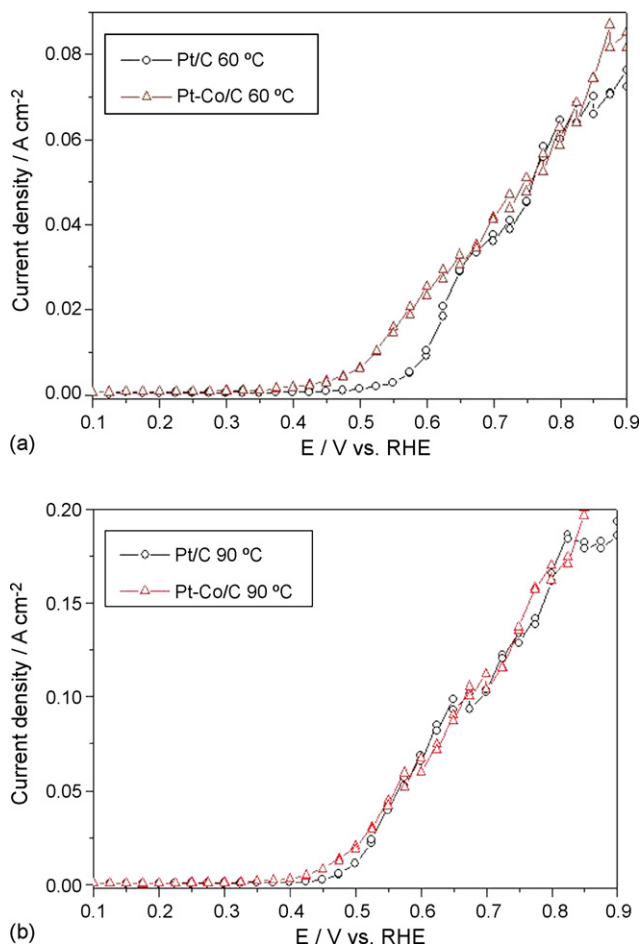


Fig. 2. Linear sweep voltammograms for ethanol oxidation on E-TEK Pt/C and Pt-Co/C electrocatalysts in  $1.0 \text{ mol L}^{-1}$  ethanol solution at (a) 60 and (b) 90 °C.

60, 80, 90 and 100 °C are shown in Fig. 3, with the current density expressed in  $\text{A mg}^{-1} \text{ Pt}$  (that is in terms of mass activity (MA)) and the numerical value is the same as that for the current expressed in  $\text{A cm}^{-2}$  (geometric area), because the Pt loading in all cases is  $1 \text{ mg cm}^{-2}$ . The cell with Pt-Co/C as cathode material performed better than the cell with Pt/C at all operational temperatures. The enhancement of the performance of the cell with Pt-Co/C is more pronounced when the current density is expressed in terms of the specific activity (SA, obtained dividing the current density expressed in terms of mass activity by the roughness factor shown in Table 1), that is in  $\text{A cm}^{-2}$  of specific Pt surface area. The results are shown in Fig. 4, at cell temperatures of 60 and 100 °C. The reason for using two different ways of expressing the current is that the MA has practical implications, because the cost of the electrode depends on the amount of Pt used, while the SA is more appropriate to compare the intrinsic activity of the different catalysts for the ORR.

The values of the maximum power density (MPD) of cells with Pt/C and Pt-Co/C as cathode materials operating at various temperatures are reported in Fig. 5 in terms of MA. As can be seen in Fig. 5, the MPD of the cells with Pt-Co/C was always higher than those with Pt/C, particularly at 100 °C when the MPD of the cell with Pt-Co/C was 30% higher than that of the cell with Pt/C.

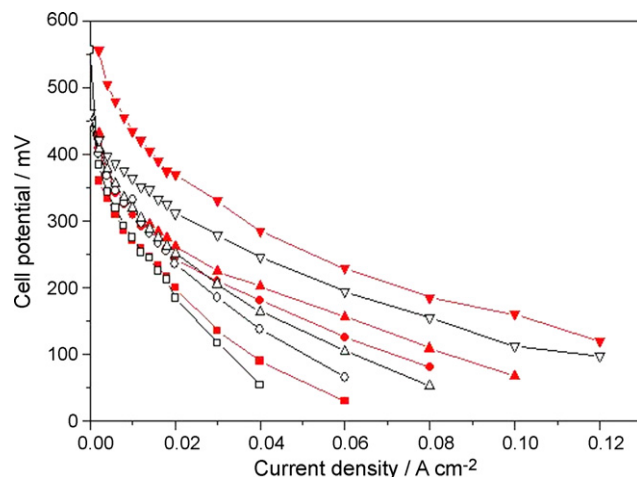


Fig. 3. Polarization curves in a single DEFC with E-TEK Pt-Co/C (3:1) and Pt/C electrocatalysts as cathode materials for oxygen reduction at 60, 80, 90 and 100 °C and 3 atm  $\text{O}_2$  pressure using a  $1 \text{ mol L}^{-1}$  ethanol solution. Cathode Pt loading  $1 \text{ mg cm}^{-2}$ . Anode: 20 wt.% Pt/C, Pt loading  $1 \text{ mg cm}^{-2}$ . ( $\square$ ) 60 °C; ( $\circ$ ) 80 °C; 90 °C; ( $\Delta$ ) 100 °C; ( $\nabla$ ). Full symbols: Pt-Co/C; open symbols: Pt/C. Currents are expressed in terms of mass activity (MA) (numerically equal to the current normalized with respect to the geometric surface area).

Fig. 6 shows the current density at 360 mV ( $\ln j_{360 \text{ mV}}$ ) versus  $1/T$ . The activation energy  $\Delta E$ , evaluated from these Arrhenius plots, is  $28 \text{ kJ mol}^{-1}$  for Pt/C, in close agreement with values for the ORR reported in the literature [16,17]. In the case of Pt-Co/C, the points do not follow a linear relationship, but the trend of the experimental points clearly shows that the activation energy for Pt-Co/C is larger than that for Pt/C. One can only speculate on the reason for this difference, but it might be related to water management effects in the cathode catalyst layer (i.e. flooding).

In view of the fact that Pt-Co/C and Pt/C have the same ethanol tolerance, the improvement in the cell performance can be ascribed to the higher ORR activity of the alloy catalyst.

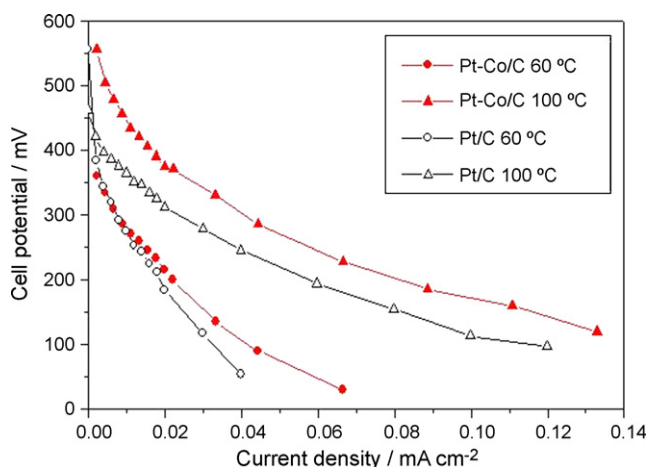


Fig. 4. Polarization curves in single DEFCs with E-TEK Pt-Co/C (3:1) and Pt/C electrocatalysts as cathode materials for oxygen reduction at 60 and 100 °C and 3 atm  $\text{O}_2$  pressure using a  $1 \text{ mol L}^{-1}$  ethanol solution. Cathode Pt loading  $1 \text{ mg cm}^{-2}$ . Anode: 20 wt.% Pt/C, Pt loading  $1 \text{ mg cm}^{-2}$ . Currents normalized with respect to the Pt surface area determined by XRD (SA).

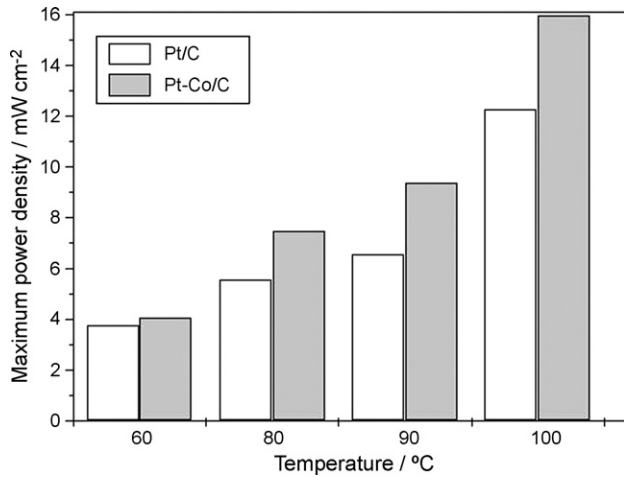


Fig. 5. Histograms of the maximum power density of direct ethanol fuel cells operating at 60, 80, 90 and 100 °C with Pt/C and Pt-Co/C (3:1) as cathode electrocatalyst.

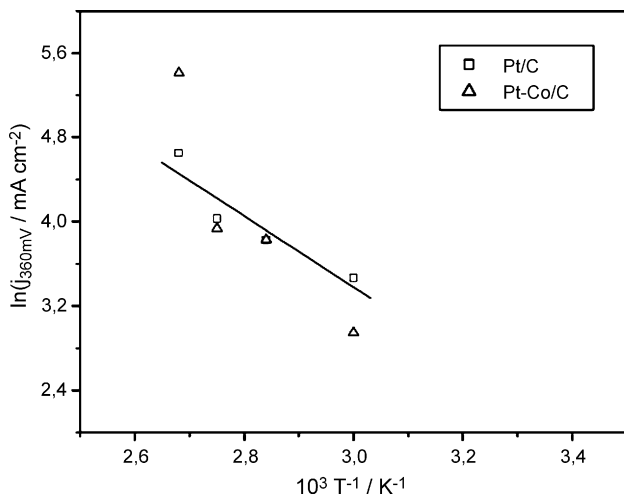


Fig. 6. Arrhenius plots for oxygen reduction on Pt and Pt-Co in direct ethanol fuel cells.

#### 4. Conclusions

Tests in DEFCs at various temperatures showed an enhancement of the cell performance when Pt-Co/C (3:1) was used as cathode material with respect to the cell with Pt/C, both in terms

of mass activity and in terms of specific activity. Considering that Pt-Co/C and Pt/C have nearly the same activity for the EOR in the cathodic potential region, i.e. the same ethanol tolerance, the improvement was ascribed to the higher activity of the binary alloy catalyst for the ORR, which manifests even in the presence of ethanol.

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