



## Effect of methanol, ethylene glycol and their oxidation by-products on the activity of Pt-based oxygen-reduction catalysts

N. Travitsky<sup>a</sup>, L. Burstein<sup>b</sup>, Y. Rosenberg<sup>b</sup>, E. Peled<sup>a,\*</sup>

<sup>a</sup> School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel

<sup>b</sup> Wolfson Applied Materials Research Center, Tel Aviv University, Tel Aviv 69978, Israel

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### ABSTRACT

Direct-oxidation fuel cells (DOFC) are promising electrochemical devices for various applications. In addition to methanol (MeOH), alternative fuels are being tested in a search for lower toxicity, safer handling, and higher energy density. Ethylene glycol (EG) was employed as one of such fuels. However, DOFCs face several problems, such as fuel crossover through the membrane during its operation. This not only lowers the cell potential but also poisons the catalyst for the oxygen-reduction reaction (ORR). Experiments were performed on the poisoning of Pt and Pt-alloy ORR catalysts (both commercial and homemade, by electroless deposition), by fuels and their oxidation by-products. At 25 °C, methanol poisoning was found to be reversible and the catalytic activity measured afterwards in a fuel-free solution and the electrochemical surface area (ECSA) were enhanced. The effect of poisoning by methanol and ethylene glycol and their oxidation intermediates is reported here for the first time. The severity of poisoning was found to be MeOH  $\ll$  formaldehyde  $<$  formic acid. In solutions of EG and its oxidation by-products, the poisoning order was EG  $\leq$  glycolic acid  $<$  oxalic acid, the poisoning of all three being more severe than that of methanol. The catalysts most resistant both to MeOH and EG poisoning were commercial acid-treated PtCo and homemade PtCoSn. The reasons for the enhanced tolerance were investigated and PtCoSn was found to be the less active both in the methanol and ethylene glycol oxidation processes.

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### 1. Introduction

Direct methanol fuel cells (DMFCs) are promising electrochemical power generators for a variety of applications. Up to now, methanol has been found to be the best fuel for DOFCs. However, methanol is toxic, highly flammable and has a tendency to pass through the fuel-cell membrane. Therefore finding alternative fuels to MeOH is very important. To replace MeOH in DOFCs, one must look for a fuel with the following characteristics: low to no toxicity, safe handling, and high capacity density. Moreover, an appropriate fuel would be one that is oxidized completely to CO<sub>2</sub> with no (or few) by-products, has a high boiling point (to be used at  $T > 100$  °C at near ambient pressure) and should be commercially available and inexpensive. Ethylene glycol (EG), on the other hand, is a safer (bp 198 °C) and a more efficient fuel (its theoretical capacity is 20% higher than that of methanol in terms of Ah ml<sup>-1</sup> –4.8 and 4, respectively). Several studies have been conducted on the EG-oxidation mechanism. Regardless of the EG utilization efficiency, in all the research the main fuel-oxidation by-products were found to be glycolic acid (GA) and oxalic acid (OA) [1,2].

The potential problem during the operation of a DOFC is fuel crossover through the membrane; this not only lowers the cell potential but also poisons the cathode catalyst. Both methanol and ethylene glycol found at the cathode can be oxidized by the Pt catalyst, lowering its activity towards oxygen reduction. Fuel-oxidation by-products, such as glycolic and oxalic acids in DEGFCs [3] and formaldehyde and formic acid in DMFCs [4–8] can also interfere with the cathode catalyst. Thus, it is necessary to develop catalysts with higher tolerance to fuel poisoning.

Non-platinum alloys, such as Pd-3D transition metal alloys at the alloy composition of ca. 60 at.% Pd were reported as methanol-tolerant, showing superior ORR activity to Pt in the presence of MeOH, despite their lower ORR activities in methanol-free solutions compared to platinum catalysts [9].

Platinum chalcogenide catalysts were found to be the most selective for the ORR in the presence of methanol [10,11]. The major disadvantage of these catalysts is their low activity compared to that of the state-of-the-art carbon-supported platinum catalysts. Carbon-supported rhodium sulfide and ruthenium–selenium catalysts exhibited oxygen-reduction activity approaching that of platinum at potentials 150 and 80 mV more negative and the ability to maintain their oxygen-reduction activity in the presence of methanol [12]. Se–Ir chalcogenide catalysts were also methanol-tolerant but had ORR activity lower than that of Pt catalysts [13].

\* Corresponding author. Tel.: +972 3 6408438; fax: +972 3 6414126.

E-mail address: [peled@post.tau.ac.il](mailto:peled@post.tau.ac.il) (E. Peled).

Platinum-macrocyclic cocatalysts are another type of catalyst with high methanol tolerance. It was found that heat-treated carbon-supported iron tetraphenylporphyrin and platinum (FeTPP-Pt/C) cocatalysts exhibited a slightly lower catalytic activity for the oxygen-reduction reaction as compared to Pt/C and lower reactivity for the methanol-oxidation reaction (MOR) [14]. Heat-treated carbon-supported cobalt phthalocyanine (CoPc) catalysts showed good resistance to methanol poisoning but were also less active towards the ORR than were carbon-supported platinum catalysts [15].

Platinum-alloy catalysts were also found to be less affected by methanol poisoning than were pure platinum catalysts [16–18]. The proposed explanation was that the lower activity of the binary electrocatalysts for methanol oxidation arises from a composition effect [16]. In a recent review by Antolini et al. [19] on platinum-based methanol-resistant ORR catalysts, Pt–Fe, Pt–TiO<sub>x</sub>, Pt–Cr, Pt–Ni, Pt–Co, Pt–CuO and Pt–Rh were mentioned as less influenced by methanol poisoning than were pure platinum catalysts. Higher MeOH tolerance can be achieved in different ways: the binary catalyst may have lower MOR activity than platinum, or higher MOR activity than Pt (thus reducing the CO poisoning) or higher ORR activity than Pt with the same MOR.

The use of platinum-based alloy catalysts with added transition metals reduces the cathode-activation losses of the polymer-electrolyte fuel cell (PEFC) caused by the comparatively sluggish kinetics of the ORR, and this leads to catalyst activity higher than that of the pure platinum catalysts [20–25].

In a search for active, fuel-poisoning-tolerant, stable catalysts we have synthesized and characterized carbon-supported PtCoNi and PtCoSn catalysts with 20% (w/w) total metal by the use of electroless deposition. Catalysts post-treated in acid had a platinum-skin structure. Catalyst powders were characterized by XRD, XPS, cyclic voltammetry and rotating-disc-electrode measurements. Experiments on fuel poisoning of synthesized and commercial platinum and platinum-alloy catalysts were performed in sulfuric acid solutions containing methanol, formaldehyde, formic acid, ethylene glycol, glycolic acid and oxalic acid. The effect of poisoning by the fuels and their oxidation by-products is reported here for the first time.

## 2. Experimental

### 2.1. Catalyst preparation

The preparation of the 20% (w/w) total metal, Vulcan XC-72 (Cabot) carbon-black-supported catalysts was carried out by a classic electroless deposition process that included the activation of a carbon-powder surface. (This process has been described elsewhere [26].) Part of the catalytic powder obtained was treated in 1 M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 15 h in order to obtain stable catalysts with platinum-skin structure. Only acid-treated homemade catalysts were tested for resistance to fuel poisoning. Commercial PtCo 20% (w/w)/XC-72-supported catalyst (E-TEK) was also acid-treated in order to compare it with the homemade catalysts.

### 2.2. Catalyst characterization

X-ray-diffraction (XRD) analysis was carried out with the use of a Theta-Theta Scintag powder diffractometer equipped with a Cu K $\alpha$  source ( $\lambda = 1.5406 \text{ \AA}$ ) and a liquid-nitrogen-cooled germanium solid-state detector. The mean size of coherent scattering domains ("grain" size) of the catalyst powders was estimated by the Scherrer equation [27] for the width of the (1 1 1) Bragg reflection, corrected for instrumental broadening.

XPS analysis was performed with a Philips UHV-5600 apparatus with an Al K $\alpha$  emission source.

### 2.3. Electrode preparation and characterization

Cyclic-voltammetry and rotating-disc-electrode tests were performed in a three-compartment glass cell, with a Ag/AgCl/3 M KCl reference electrode in a Luggin capillary compartment and a Pd-wire counter electrode. All potentials, however, are reported in terms of the reversible-hydrogen-electrode (RHE) scale. The working electrode was a 5-mm-diameter glassy-carbon-disc rotating electrode (Pine Instruments, USA) covered by catalytic ink with platinum loading of  $\sim 15 \mu\text{g cm}^{-2}$ . Carbon-supported catalysts were applied on polished glassy-carbon disks by transferring 10 ml of a sonicated catalyst ink, consisting of 10 mg catalyst powder, 72  $\mu\text{l}$  Nafion solution 5% (w/w), 3 g H<sub>2</sub>O and 2 g ethanol. All electrochemical experiments were carried out with the use of an Eco Chemie (Netherlands) AUTOLAB potentiostat at room temperature ( $23 \pm 2 \text{ }^\circ\text{C}$ ).

Tests for the estimation of electrochemically active surface area (ECSA) were carried out in a quiescent 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Nitrogen was bubbled into the solution for 30 min before the measurements and passed over the solution during the scan. The cell was cycled between 0 and 1 V at a  $20 \text{ mV s}^{-1}$  sweep rate, for a total of five scans. The voltammograms were reproducible from the second scan on. The electrochemical surface area of platinum was determined from the coulometric charge in the hydrogen-desorption region, under the assumption of  $210 \mu\text{C cm}^{-2}$  of hydrogen adsorbed [28]. All values of ECSA are normalized to platinum loading [ $\text{m}^2 \text{ g}^{-1}(\text{Pt})$ ].

RDE experiments were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, into which O<sub>2</sub> was bubbled. The cell was cycled between 0 and 0.8 V at a  $5 \text{ mV s}^{-1}$  sweep rate, 2500 rpm rotation rate, for total of four scans. The current density for the oxygen-reduction reaction during the last anodic sweep was a measure of the catalyst activity. The kinetic current was found as follows [29]:

$$i_k = \frac{i_d \cdot i}{i_d - i}$$

where  $i$  is the experimentally obtained current density from the polarization curve,  $i_d$  refers to the measured diffusion-limited current density, and  $i_k$  is the mass-transport-free kinetic current. The currents were measured at two potentials, 0.9 and 0.85 V. The potential of 0.9 V is a benchmark for catalyst-activity measurements, since in this region, mass-transport corrections are valid [30]. However, current densities at this potential are very low, so we measured catalyst activity at 0.85 V as well. During the poisoning experiments, the measured current at 0.9 V sometimes turned positive as a result of the high oxidation currents, so that only the results at 0.85 V are presented. Kinetic currents normalized to platinum weight are mass activities (MA) and currents normalized to the electrochemically active surface areas are specific activities (SA).

Experiments on fuel poisoning were conducted in the following solutions: 10 mM MeOH, 10 mM formaldehyde, 10 mM formic acid, 10 mM EG, 10 mM GA, 10 mM OA. A concentration of 10 mM was chosen as sufficient for a quantifiable poisoning effect but not so high that oxidation currents prevail over reduction currents. In all the experiments the electrolyte was 0.5 M H<sub>2</sub>SO<sub>4</sub>. Prior to cycling in the fuel solution, the surface area of the catalysts and their electrochemical activity were estimated in pure sulfuric acid solution. Between measurements, the electrodes were washed thoroughly and circulated for 10 min in distilled water in order to decrease the effect of the previous solution.

Oxidation measurements on methanol and ethylene glycol were performed in 1 M solutions at 60 °C.

**Table 1**  
Commercial and homemade catalysts physical and electrochemical characterization.

	Pt E-TEK	PtCo E-TEK	PtCo E-TEK acid-treated	PtCoSn homemade acid-treated	PtCoNi homemade acid-treated
Grain size (nm)	2.3	3.2	3.1	2.6	2.5
ECSA ( $\text{m}^2 \text{g}^{-1}$ )	93	81	62	66	61
Composition by EDS	Pt	Pt <sub>48</sub> Co <sub>52</sub>	Pt <sub>80</sub> Co <sub>20</sub>		Pt <sub>78</sub> Co <sub>15</sub> Ni <sub>7</sub>
Surface composition (by XPS)	Pt	Pt <sub>45</sub> Co <sub>55</sub>	Pt <sub>100</sub> Co <sub>0</sub>	Pt <sub>74</sub> Co <sub>0</sub> Sn <sub>26</sub>	Pt <sub>100</sub> Co <sub>0</sub> Ni <sub>0</sub>
Bulk composition (by XPS after sputtering)	Pt	Pt <sub>50</sub> Co <sub>50</sub>	Pt <sub>83</sub> Co <sub>17</sub>	Pt <sub>78</sub> Co <sub>10</sub> Sn <sub>12</sub>	Pt <sub>86</sub> Co <sub>3</sub> Ni <sub>11</sub>

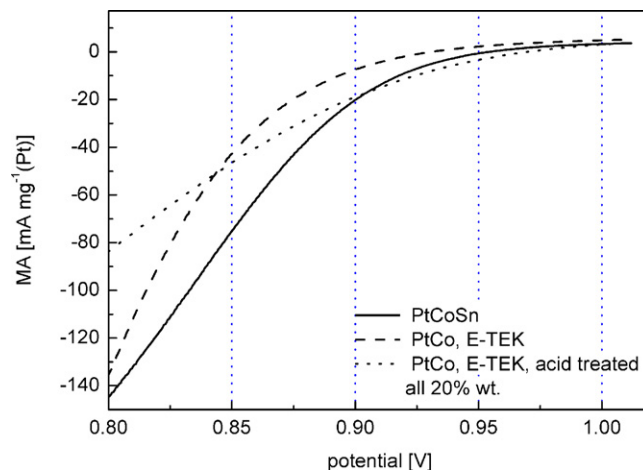
### 3. Results and discussion

The grain size of both homemade and commercial catalysts was measured by XRD and their surface and bulk composition was determined by XPS analysis (Table 1). The surface of the treated samples was highly enriched in platinum in all the catalyst powders and no cobalt was found on the surface. While the commercial PtCo catalyst and homemade PtCoNi acquired a pure platinum skin after the acid treatment, in PtCoSn the surface composition was Pt<sub>74</sub>Sn<sub>26</sub>. Corrosion of cobalt and nickel during the acid treatment takes place on the surface of the catalyst particles, thus leaving a pure or almost pure platinum “skin”. These “skin”-type catalysts are highly catalytic for the ORR reaction [25,31]. XPS analysis of the inner layers after sputtering of the samples showed that the concentration of the alloying metal increases sharply inside the sample and approaches the value given by EDS for the bulk concentration (Table 1). If it is taken into account that XPS measurement of the sputtered sample provides an “average” of both the bulk and the surface concentrations of the powder particles, the sample composition should lie between the values given by EDS and XPS of the untreated sample. The corrosion resistance of the PtCoSn and PtCoNi was not tested but 60% (w/w). PtCo and PtNi catalysts synthesized by the same procedure were found to be stable in 1 M H<sub>2</sub>SO<sub>4</sub>, at 80 °C after the three-hour acid treatment as published in our previous work [26]. The grain size of synthesized alloy catalysts was close to that of the commercial platinum catalyst and slightly smaller than that of E-TEK PtCo catalyst. Thus, the effect of catalyst size on fuel tolerance may be neglected and only their compositional and structural differences will be responsible for the different poisoning behavior.

As expected, the ORR catalytic activity of the acid-treated alloy powders was higher than that of the commercial platinum catalyst with the same metal loading. The PtCoSn homemade acid-treated catalyst showed higher activity in rotating-disc measurements than did the commercial PtCo catalyst (Fig. 1). The activity of acid-treated E-TEK catalyst was comparable to that of the PtSnCo catalyst and the activity of the as-received sample was similar to that of PtCoNi. The CV curves of all the catalysts (except for homemade PtCoNi—for reasons of space-saving) are presented in Fig. 2. Alloy catalysts, both synthesized and commercial, after treatment in acid, have similar ECSAs in the range of 60  $\text{m}^2 \text{g}^{-1}$  (Table 1). The surface area of PtCo E-TEK catalyst decreased as a result of corrosion of the amorphous regions and further recrystallization and agglomeration [26]. The ECSA of Pt E-TEK catalyst is higher than those of the alloys.

#### 3.1. Catalyst poisoning by methanol and its oxidation by-products

Commercial Pt, PtCo, acid-treated PtCo catalysts and homemade PtCoSn and PtCoNi catalysts were tested for methanol, formalde-

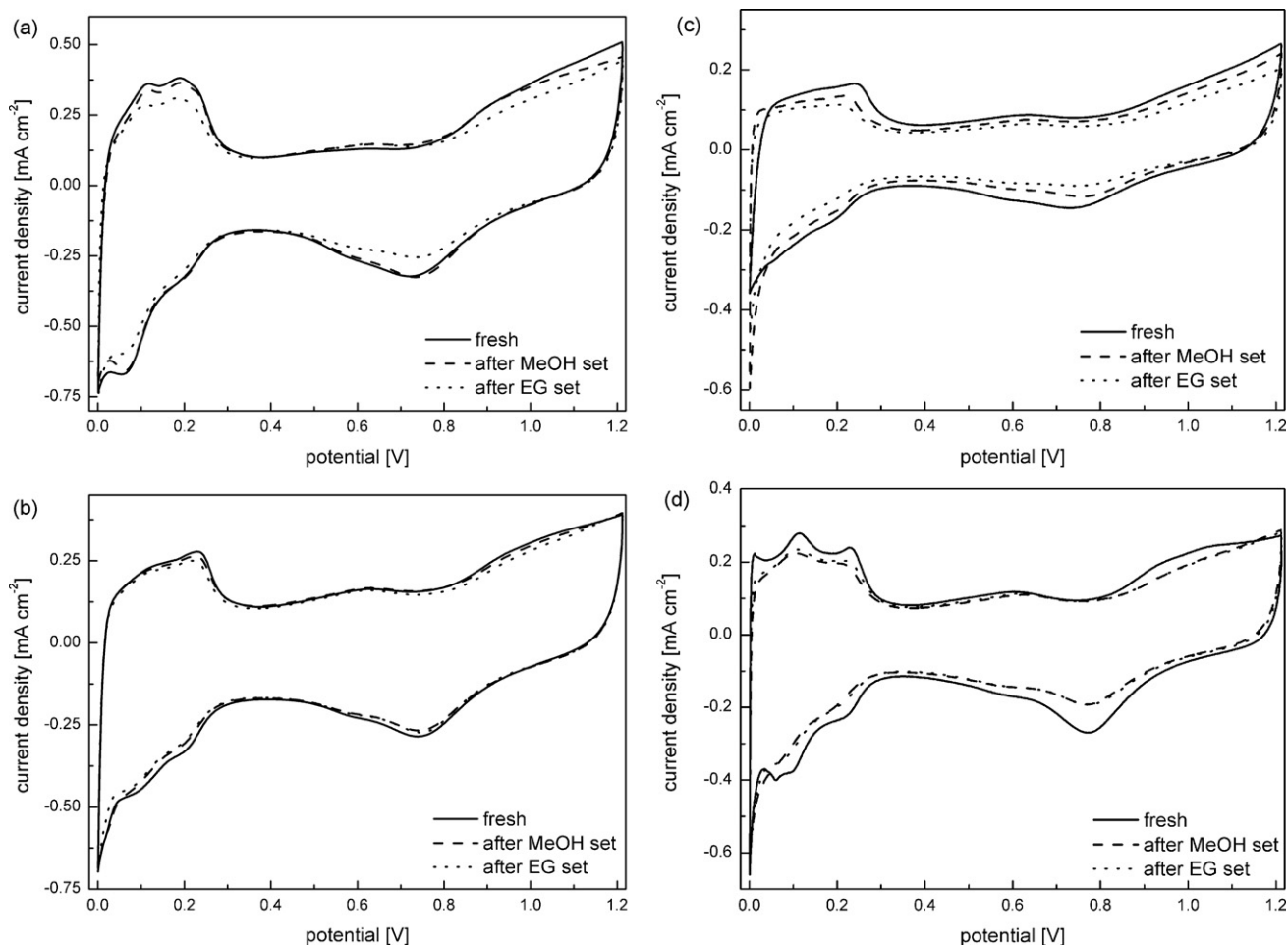


**Fig. 1.** RDE measured ORR mass activity of 20% (w/w)/XC-72 PtCoSn, PtCo and PtCo acid treated catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

hyde and formic acid tolerance. The fuels affect the ORR in two different ways: (1) fuel oxidation on the ORR catalyst or a direct redox reaction between fuel and oxygen (current thief leading to consumption of oxygen at the catalyst surface) and (2) consequent lowering of free  $\theta_{\text{Pt}}$  due to fuel and its oxidation by-product adsorption on the catalyst that lower the ORR exchange current density. In all the catalysts, the change in the severity of poisoning was in the following order: methanol  $\ll$  formaldehyde  $<$  formic acid (Figs. 3 and 4a and b). This can be explained by the thermodynamic characteristics of the oxidation of these three substances. While the oxidation of methanol to formaldehyde is the rate-determining step of the three-step MeOH oxidation process, formic acid is the easiest to oxidize among these three species [32]. Thus, formic acid has the greatest poisoning effect, since its oxidation reaction competes with ORR, sometimes even leading to positive currents (on the PtCo catalyst, for example). In addition, among the three substances, formic acid would appear to have the strongest adsorption energy on the platinum surface. This because formic acid and not methanol and formaldehyde, can form a bidentate complex on the catalyst surface leading to large decrease of free  $\theta_{\text{Pt}}$ . It should be noted, that the different order of insertion of poisoning solutions did not affect the order of severity of poisoning—PtCoSn catalyst was once first tested in a solution of formic acid and afterwards in formaldehyde, but the activity in formaldehyde was still higher than in formic acid. Thus, formic acid is more poisonous than formaldehyde and methanol. The activity of a catalyst in a fuel and in solutions of the fuel and its oxidation by-products was proportional to the initial activity of the fuel. The higher the activity in

**Table 2**  
MA [ $\text{A mg}^{-1}(\text{Pt})$ ] of catalysts at 0.85 V in different solutions (presented values are averages of at least three measurements).

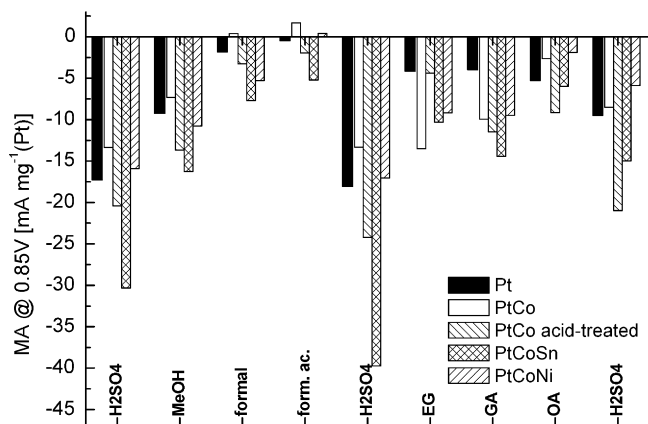
	Pt E-TEK	PtCo E-TEK	PtCo E-TEK acid-treated	PtCoSn homemade	PtCoNi homemade acid-treated
Fresh H <sub>2</sub> SO <sub>4</sub>	17.3	13.4	20.4	30.3	15.9
After MeOH set	18.0	13.3	24.2	39.7	17.0
After EG set	9.5	8.5	21.0	15.0	5.9



**Fig. 2.** (a) Cyclic voltammogram of commercial Pt 20% (w/w)/XC-72 catalyst measured in 0.5 M  $\text{H}_2\text{SO}_4$ : fresh electrode, after being tested in methanol, formaldehyde, formic acid and after being tested in ethylene glycol, glycolic acid and oxalic acid. (b) Cyclic voltammogram of commercial PtCo 20% (w/w)/XC-72 catalyst measured in 0.5 M  $\text{H}_2\text{SO}_4$ : fresh electrode, after being tested in methanol, formaldehyde, formic acid and after being tested in ethylene glycol, glycolic acid and oxalic acid. (c) Cyclic voltammogram of commercial PtCo 20% (w/w)/XC-72 acid treated catalyst measured in 0.5 M  $\text{H}_2\text{SO}_4$ : fresh electrode, after being tested in methanol, formaldehyde, formic acid and after being tested in ethylene glycol, glycolic acid and oxalic acid. (d) Cyclic voltammogram of homemade PtCoSn 20% (w/w)/XC-72 catalyst measured in 0.5 M  $\text{H}_2\text{SO}_4$ : fresh electrode, after being tested in methanol, formaldehyde, formic acid and after being tested in ethylene glycol, glycolic acid and oxalic acid.

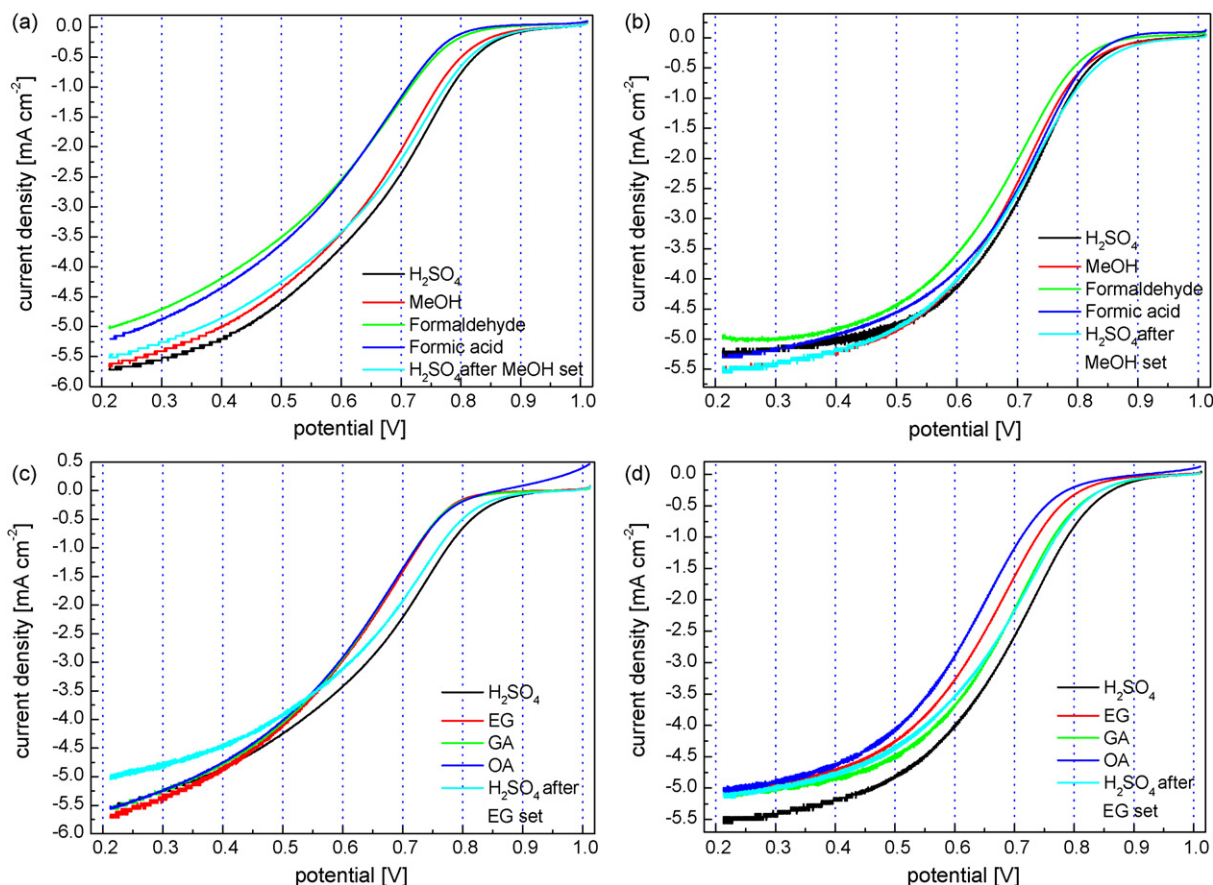
the pure acid, the more tolerant the catalyst was to methanol oxidation (Fig. 3). The highest reduction currents were obtained with the homemade PtCoSn catalyst. Commercial PtCo acid-treated catalyst had the second-best activity. The least-tolerant catalyst was the as-received E-TEK PtCo. The decrease in catalyst activity was

gradual, with each fuel solution further lowering the ORR current density. The PtCoNi catalyst was relatively stable in MeOH and formaldehyde solutions, similar to the behavior of the PtCoSn, but its activity was significantly depressed in formaldehyde. After the series of measurements in solutions of methanol and its derivatives, the activities of the ORR catalysts were measured once again in pure sulfuric acid solution in order to examine the reversibility of poisoning. The electrochemical surface area was estimated as well (Table 3, Fig. 2). It was found that all the catalysts not only retained their initial activity but both the mass and surface activities were enhanced (Table 2, Fig. 4a). The catalytic surface areas were significantly lowered only in Pt and PtCo E-TEK catalysts, while ECSA of homemade PtCoSn and of E-TEK acid-treated PtCo were sustained. Thus, poisoning by methanol and its oxidation by-products is reversible and rinsing in water restores catalyst activity and surface area. Methanol and its derivatives can reduce the content of platinum oxides on the surface of the cathode catalyst at high potentials, cleaning and enhancing the catalyst surface. The same result is achieved during air starvation in the operating fuel cell, when the oxygen flow to the cathode is stopped and methanol, which has passed to the cathode compartment as a result of crossover, reduces platinum oxides and the cell performance is improved [33,34]. In addition, the reversibility of the poisoning can be explained by the relatively rapid oxidation reactions of the by-products, which do



**Fig. 3.** Graphical representation of ORR mass activities in all the tested solutions on Pt, PtCo, PtCo acid-treated and PtCoSn catalyst.





**Fig. 4.** (a) RDE measured ORR mass activity of commercial Pt 20% (w/w)/XC-72 catalyst measured in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M methanol, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M formaldehyde and 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M formic acid. (b) RDE measured ORR mass activity of homemade PtCoSn 20% (w/w)/XC-72 catalyst measured in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M methanol, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M formaldehyde and 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M formic acid. (c) RDE measured ORR mass activity of commercial Pt 20% (w/w)/XC-72 catalyst measured in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M EG, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M GA and 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M OA. (d) RDE measured ORR mass activity of homemade PtCoSn 20% (w/w)/XC-72 catalyst measured in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M EG, 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M GA and 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M OA.

not stay adsorbed on the catalyst surface, but are oxidized and removed.

### 3.2. Catalyst poisoning by ethylene glycol and its oxidation by-products

After the set of methanol-poisoning experiments, the rinsed catalysts were tested for ethylene glycol, glycolic acid and oxalic acid tolerance. Since initial activities were retained, there was no need to prepare new electrodes and the behavior of the same catalyst in different solutions could be investigated on the same electrodes. For all catalysts except for untreated E-TEK PtCo, ethylene glycol decreased catalytic activity more than did glycolic acid (Figs. 3 and 4c and d). Oxalic acid was found to be the most poisonous species. Here the poisoning mechanism is different—the most poisonous species being the one which is hardest to oxidize, thus being strongly adsorbed on the catalyst surface. In the EG oxidation reaction mechanism, oxidation of EG to GA through glycol aldehyde is considerably faster than GA oxidation to OA through glyoxylic acid, making OA the hardest intermediate to oxidize [1,35]. So the oxidation of oxalic acid's by-products is slower than that of ethylene glycol's, leading to strongly adsorbed species, preventing oxygen adsorption and reduction. This conclusion is also supported by the fact that no positive currents are obtained. This means that considerable oxidation does not take place but the ORR activity is diminished for another reason. Again, as in the case of formic acid lower catalysts activity in GA and OA containing solutions could result from the formation of bidentate complex on the cata-

lyst surface. These complexes have higher bonding strength, which could lead to a large decrease of the free  $\theta_{Pt}$  that lowers the ORR exchange current density. The poisoning effect follows the order: OA > GA ≥ EG. Here as well, the decrease in activities was proportional to their initial values except for E-TEK PtCo. Though its initial activity was rather low, it sustained almost the same activity in both EG and GA solutions, indicating lower adsorption of EG and GA on this catalyst. In OA its tolerance was reduced. The platinum catalyst was affected by all the three substances in a very similar way, in contrast to all the other catalysts. The most tolerant catalysts in these poisoning series were PtCoSn and acid-treated E-TEK PtCo, with PtCoSn more active in EG and GA and PtCo more tolerant to OA. The activity of E-TEK PtCo and PtCoNi were again similar. In contrast to the case of methanol poisoning, the effect of ethylene glycol and its derivatives on the catalyst activities was less reversible. Only treated PtCo retained its initial activity, while the activities of the others were lowered. ECSAs of Pt and PtCo acid treated were decreased after the catalysts were thoroughly rinsed and measured in pure acid. PtCoSn preserved its active surface and the area of the PtCo catalyst was even enhanced, as borne out by the fact that it was capable of sustaining almost its initial activity in all the poisoning solutions (Table 3, Fig. 2).

Comparing the tolerance of the catalysts to methanol and EG with their corresponding by-products, leads to conclusion that the ORR is more influenced by EG crossover than by MeOH. The same phenomenon can be observed in the working fuel cell, since the cathode overpotential in DEFC is higher than in DMFC [36]. This could be explained by the stronger adsorption and lower oxida-

**Table 3**  
ECSA [ $\text{m}^2 \text{g}^{-1}(\text{Pt})$ ] of catalysts in different solutions (presented values are averages of at least three measurements).

	Pt E-TEK	PtCo E-TEK	PtCo E-TEK acid-treated	PtCoSn homemade	PtCoNi homemade acid-treated
Fresh $\text{H}_2\text{SO}_4$	93	84	62	66	61
After MeOH set	84	61	56	64	62
After EG set	67	68	39	63	49

tion rates of GA and OA compared to EG. Thus, the by-products are strongly adsorbed on the catalyst surface, and hard to remove by rinsing with water.

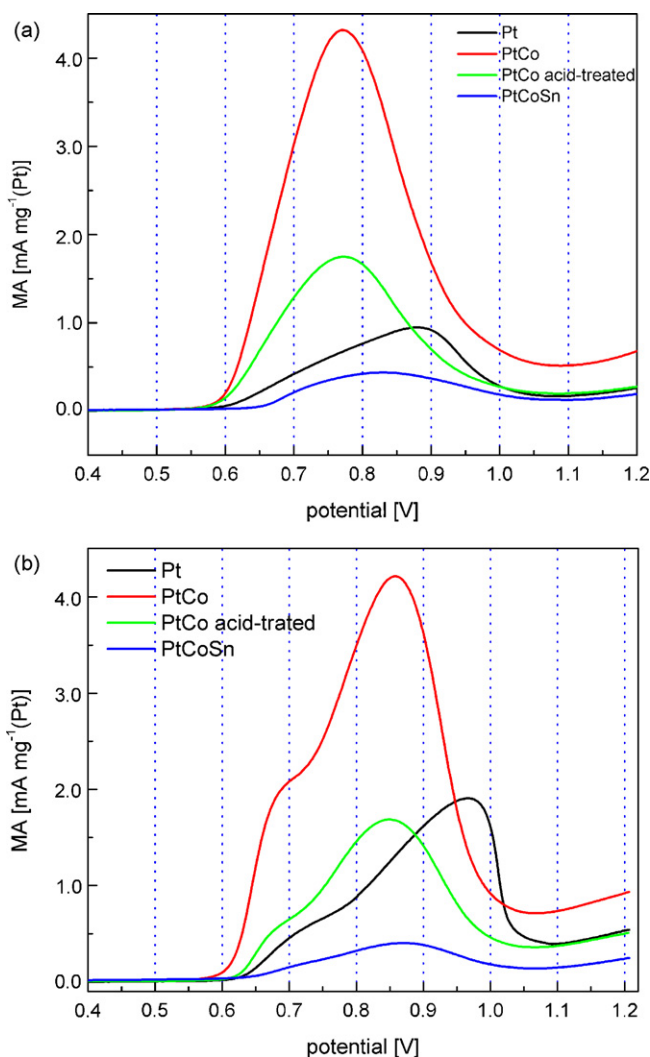
### 3.3. Methanol and ethylene glycol oxidation on ORR catalysts

One of the possible reasons for the enhanced tolerance of cathode alloy catalysts is their lower activity towards fuel oxidation compared to pure platinum. This would lead to reduced fuel adsorption on their surface, thus lessening the interference of the oxidation reaction of the fuel with the ORR. On the other hand, catalysts with higher fuel-oxidation activity can also decrease ORR-catalyst poisoning by lessening the adsorption of the fuel and its by-products on the catalyst surface as a result of its easier oxidation and removal [19]. In order to understand the difference between the tolerance of the different catalysts, methanol and ethylene glycol were oxidized on the commercial platinum and PtCo catalysts and on the homemade PtCoSn catalyst in 1 M solutions at 60 °C. Fuel-oxidation CV curves and the onset potentials of MeOH and EG oxidation are presented in Fig. 5 and Table 4, respectively. Both in MeOH and in ethylene glycol, the as-received PtCo had the lowest onset potential, the potential of the acid-treated PtCo catalyst was similar to that of platinum and a higher onset potential was obtained with PtCoSn. In both solutions, the onset potential for PtCoSn oxidation was the highest among all the catalysts, in agreement with its higher tolerance towards ORR fuel poisoning due to its lower fuel-oxidation activity. In MeOH solution, the results of the fuel-oxidation experiment are in agreement with the data on catalyst tolerance, PtCoSn being the least active catalyst towards MeOH oxidation and thus less influenced by its adsorption on the cathode catalyst. However, the second-best catalyst for poisoning tolerance in MeOH is acid-treated PtCo, while its MeOH-oxidation onset potential is close to that of platinum. However, it is higher than that of the untreated sample, in agreement with their tolerance data. In general, it can be said that the higher the onset potential for MeOH oxidation, the higher the selectivity towards oxygen reduction and the greater the reversibility of poisoning. The fact that PtCoSn is the least active towards MeOH oxidation is unexpected, as PtSn is usually used as an anode catalyst in DMFCs [37,38]. However, this can be explained by the fact that the PtSn alloy is a good catalyst for CO oxidation but not as good for methanol oxidation, as a result of the lower ability of the platinum in this catalyst to adsorb MeOH [39].

In EG-containing electrolytes, the difference in onset potentials between the two best catalysts (PtCoSn and acid-treated PtCo) is smaller than in MeOH. This corresponds to the ORR activity in the poisoning solutions—PtSnCo was more active in MeOH than in EG as compared to platinum. The oxidation onset potential of the catalysts in the EG solution follows the same order as in MeOH solutions.

**Table 4**  
Methanol and ethylene glycol onset oxidation potentials with different catalysts.

	MeOH onset potential (V)	EG onset potential (V)
Pt E-TEK	0.599	0.621
PtCo E-TEK	0.586	0.609
PtCo E-TEK, acid treated	0.595	0.624
PtCoSn homemade	0.651	0.656



**Fig. 5.** (a) Cyclic voltammogram of MeOH oxidation mass activity of commercial Pt, PtCo, PtCo acid-treated and homemade PtCoSn catalysts, all 20% (w/w)/XC-72 measured in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M MeOH, 60 °C. (b) Cyclic voltammogram of EG oxidation mass activity of commercial Pt, PtCo, PtCo acid-treated and homemade PtCoSn catalysts, all 20% (w/w)/XC-72 measured in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M EG, 60 °C.

## 4. Summary

The ORR catalytic activity of the acid-treated alloy powders was higher than that of the platinum catalysts with the same metal loading. The homemade PtCoSn catalyst showed higher activity in rotating-disc measurements than did the commercial PtCo catalyst. Catalysts post-treated in acid were found to be stable and had a platinum-rich (or pure) “skin” structure. The tolerance of synthesized and commercial catalysts for fuel poisoning was tested on a RDE in solutions containing methanol, ethylene glycol and their oxidation by-products. At 25 °C, methanol poisoning of the ORR catalysts was reversible and the catalytic activity measured afterwards in a fuel-free solution was enhanced. The severity of poisoning was found to be MeOH < formaldehyde < formic acid. The

severest poisoning species among EG and its derivatives was oxalic acid. The catalysts most resistant both to MeOH and EG poisoning were commercial acid-treated PtCo (surface composition: Pt<sub>100</sub>Co<sub>0</sub>) and homemade PtCoSn (surface composition: Pt<sub>74</sub>Co<sub>0</sub>Sn<sub>26</sub>). Consequently, the most appropriate catalysts for MeOH and EG tolerance among those tested are the skin-type catalysts, while Sn on the catalyst surface slightly enhances the tolerance (PtCoSn compared to acid-treated PtCo) and Co decreases it (PtCo compared to acid-treated PtCo). We have proved that the PtCoSn catalyst is more tolerant for MeOH and EG poisoning than is the platinum catalyst as a result of its lower fuel-oxidation activity, despite sufficient presence of tin on the surface. Both in MeOH and in EG, the higher the catalyst activity in the ORR and the higher the fuel-oxidation onset potential, the more tolerant the catalyst was to fuel poisoning. In addition, it was found, in agreement with the DOFC data, that poisoning by MeOH and its by-products was more reversible than that of EG.

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