Methanol tolerant electrocatalysts for the oxygen reduction reaction

M. Asteazaran · S. Bengió · W. E. Triaca · A. M. Castro Luna

Abstract Direct methanol fuel cells (DMFCs) represent an interesting alternative in obtaining electricity in a clean and efficient way. Portable power sources are one of the most promising applications of passive DMFCs. One of the requirements in these devices is to use high alcohol concentration, which due to methanol crossover causes a considerable loss of fuel cell efficiency. In order to develop methanol tolerant cathodes with suitable activity, different supported catalysts namely PtCo/C and PtCoRu/C, were prepared either via ethylene glycol reduction (EG) with or without microwave heating assistance (MW) or via the alloy method, the latter followed by a thermal treatment in a reducing atmosphere (N_2/H_2). All cathode-catalysts were tested to determine the role of the components in simultaneously enhancing the oxygen reduction reaction (ORR) and discouraging the methanol oxidation reaction. According to the synthesis methodology, X-ray photoelectron spectra showed that the amount of metal oxides on the surface varies, being higher on the PtCo/C EG and PtCoRu/C EG catalysts. The electrochemical characterization of the catalysts was accomplished in a three electrodes electrochemical cell with a glassy carbon rotating disk electrode covered with a thin catalytic film as working electrode. To study the ORR and the influence of different methanol concentrations, linear sweep voltammetry and cyclic voltammetry were employed. The PtCo/C EG, with an important metal oxide amount on the surface, and the PtCoRu/C MW and EG electrodes, both with RuO_2 on their surfaces, were the most tolerant to methanol presence.

Keywords ORR · PtCo/C · PtCoRu/C · Methanol crossover · DMFC · Methanol-tolerant cathode catalysts

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1 Introduction

Direct methanol fuel cells (DMFCs) are an interesting alternative to obtain electricity in a clean and efficient way to substitute traditional environmentally harmful energy sources [1, 2].

One of the most promising applications of DMFCs is as power source in portable devices. In particular, passive alcohol fuel cells using high alcohol concentration have been proposed [3, 4].

Unfortunately, methanol permeation across the polymer electrolyte membrane (methanol crossover) causes a considerable loss of efficiency in the cell, because both the oxygen reduction reaction (ORR) and the methanol oxidation reaction (MOR) occur simultaneously at the cathode.

Numerous attempts have been proposed to find a solution to the problem by either synthetizing novel ion conducting membranes resistant to alcohols [5, 6] or by making electrocatalysts with high activity for the ORR and at the same time tolerant to alcohol presence [7–9]. Platinum is considered as the most active catalyst for ORR in acid media, however due to kinetic limitations of the

reaction, mostly due to Pt-oxide formation, materials with high catalytic activity are required for low temperatures fuel cells to compensate the low efficiency of the kinetic process [10, 11].

It has been claimed that by alloying platinum with certain transition metals M (M = Co, Fe, Cr, Ni) it is possible to improve the Pt activity for the ORR due to the cocatalysts causing a downward shift of the Pt d-band center with respect to the Fermi level, thus diminishing the adsorption strength of the oxygen species. The improvement for the ORR has been demonstrated with PtM alloys prepared by different procedures [11–13].

Moreover, in DMFCs, problems related to catalytic activity of the cathode are more severe since methanol competes with oxygen for the active Pt sites and a mixed potential emerges from the simultaneous occurrence of the ORR and MOR reactions. Different Pt base nanoparticles have been proposed and employed for ORR in presence of methanol [14–16]. In Ref. [17], Ocón et al. claimed that a methanol tolerant catalyst, namely PtCoRu/C, can be obtained in an operating DMFC after Ru dissolution of a PtRu anode and its subsequent deposition on the PtCo/C cathode.

The use of different procedures to synthesize metal nanoparticles supported on carbon of high surface area plays an important role in the development of fuel cell technology. Special attention should be paid not only on the catalyst composition but also on the synthesis method employed in their preparation [12, 18].

The aim of this work is to synthesize by different routes carbon supported nanoparticles of PtCo/C and PtCoRu/C as methanol tolerant oxygen reduction catalysts and to discern the causes of improvements in their methanol tolerance.

2 Materials and methods

2.1 Preparation and characterization of the catalysts

Carbon supported nanoparticles (NP) of PtCo/C and PtCoRu/C were prepared by using either (i) the classic ethylene glycol method (EG) [19] and a variation with microwave-assisted heating (MW) or (ii) the alloy method (AM), in line with Gonzalez et al. [20].

2.1.1 Classic EG and microwave heating assisted MW methods

In the classic EG, ethylene glycol is the reducing agent and dissolving medium where the synthesis occurs. Summarizing, ethylene glycol solutions of each metal precursor, H_2PtCl_6, $CoCl_2$ and $RuCl_3$, in the required amount were added in a suspension of a calculated amount of functionalized carbon black support in ethylene glycol, under vigorous stirring. The mixture was stirred for 4 h under N_2 bubbling. Once the stirring was finalized, NaOH solution in ethylene glycol was added to the mixture to adjust its pH around 13. In order to achieve complete reduction of the metallic precursors, the mixture was refluxed at 197 °C for 2 h also under N_2 bubbling. The solid was isolated by low pressure filtering, then thoroughly rinsed with water and dried at 70 °C in an oven for 12 h. The synthesized electrocatalysts were labeled as PtCo/C EG and PtCoRu/C EG. Additionally, functionalization of the support was achieved after oxidative treatment in 70 % HNO_3 solution at 140 °C for 2 h, according to the work of Bonesi et al. [21].

In the ethylene glycol microwave-assisted heating procedure (MW), PtCoRu/C MW was prepared following the method described by Almeida et al. [22]. Following this method, a calculated amount of the different precursors was added in ethylene glycol and stirred for approximately 5 min in an ultrasonic bath, and a measured amount of carbon Vulcan® XC-72R powder was then added. The mixture was kept under ultrasound stirring for 30 min, until a homogeneous suspension was obtained. This suspension was then placed in a common household microwave oven (Likon, 2.45 GHz, 700 W) and irradiated for 70 s. Finally, the suspension was filtered and washed repeatedly with water, and then dried in an oven at 80 °C for 12 h.

2.1.2 Alloy method

In the AM, the initial reactant was a given quantity of E-TEK Pt/Vulcan XC-72R, which was dispersed in water and ultrasonically stirred for 15 min. The initially acidic pH was shifted to 8 by adding an ammonium hydroxide solution. At this point, the required amount of $CoCl_2$, in order to obtain the compositions listed in Table 1, was put into the mixture and then, a HCl solution was added to reach a pH of 5.5. Stirring continued for 1 h and then the solid was isolated by filtering, rinsing with water repeatedly and finally drying at 70 °C in an oven for 12 h. After that, the powder was heat-treated at 900 °C in a H_2/N_2 atmosphere for 1 h to form a binary alloy catalyst. The synthesized electrocatalysts were labeled as PtCo/C AM.

2.2 Catalysts characterization

2.2.1 Physicochemical characterization

All synthesized materials were studied in terms of composition and surface chemistry by using energy-

Table 1 Summary of the properties of the investigated catalysts

Synthesis method	Pt/Co at. ratio[a]	Pt/Ru at. ratio[a]	Catalyst label	SA[b] [mA cm ^{2}]	MA[c] [Amg$_{Pt}^{-1}$]	ECSA[d] [m^{2}g$_{Pt}^{-1}$]	Onset ORR[e] [V]
EG	5.2		Pt_5Co EG	0.18	0.07	40.06	0.837
AM	5.3		Pt_5Co AM	0.24	0.19	79.79	0.867
EG	10.1		$Pt_{10}Co$ EG	0.12	0.06	49.86	0.842
AM	10.4		$Pt_{10}Co$ AM	0.33	0.30	90.66	0.875
EG	3.1	1.1	PtCoRu EG	0.11	0.05	44.68	0.829
MW	8.3	1.2	PtCoRu MW	0.19	0.11	58.92	0.859

[a] Determined from EDS analysis

[b] Specific activity for ORR in an O_2 saturated 0.5 M H_2SO_4 calculated at 0.8 V

[c] Mass activity for ORR in an O_2 saturated 0.5 M H_2SO_4 calculated at 0.8 V

[d] Electrochemically active surface area

[e] Onset potential for ORR determined from Fig. 2

dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

For the surface composition analysis via XPS a standard Al/Mg twin anode X-ray gun and a hemispherical electrostatic electron energy analyzer were used. For the analysis, the powdered samples were spread on an adhesive carbon tape and the C 1 s peak at 284.5 eV was used as reference to calibrate the binding-energy scale.

2.2.2 *Electrochemical characterization*

The electrochemical characterization was accomplished by employing a standard three-electrode electrochemical cell. We used as a working electrode a rotating disk electrode (RDE) of glassy carbon (0.071 cm^2 geometric area) covered with a thin layer of catalyst powder (28 μg cm^{-2} Pt loading), attached by a Nafion® thin film [23]. A Pt foil of 1 cm^2 geometric area was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. In this work, we refer all potentials to that of the reversible hydrogen electrode (RHE). The supporting electrolyte used was 0.5 M H_2SO_4 and the working solution was an O_2 saturated 0.5 M H_2SO_4 solution containing different CH_3OH concentrations. The electrochemical experiments were conducted at room temperature. Prior to all experiments, we cycled the potential of the working electrode between 0.05 and 1.10 or 0.8 V (depending on the catalyst composition) at a rate of 0.1 Vs^{-1} in a N_2 purged 0.5 M H_2SO_4 solution in order to get a stable voltammetric profile.

The electrochemically active surface area of each working electrode, listed in Table 1, was then determined by integrating the charge required for stripping a pre-adsorbed monolayer of CO at 0.05 V, taking into account that 420 μC is equivalent to 1 cm^2.

3 Results and discussion

3.1 Physicochemical characterization

3.1.1 *EDS analysis*

The atomic percentages of the components in PtCo/C and PtCoRu/C EG, MW and AM catalysts, listed in Table 1, were determined by EDS. It can be highlighted that EDS is a surface technique that goes through <1 μm whereas XPS measures the elemental composition of the surface from the top to 4 nm in depth.

3.1.2 *XPS analysis*

The surface composition of the catalysts was determined measuring the Pt 4f, Co 2p and Ru 3d photoelectron peaks. The XPS spectra of Pt based catalysts Pt_5Co/C AM, Pt_5Co/C EG, PtCoRu/C MW and PtCoRu/C EG obtained in the region of Pt 4f core level, are shown in Fig. 1a, b, c and d, respectively. Each of these elemental spectra is composed of two identical peaks that correspond to the spin–orbit split 4f 7/2 and 4f 5/2 of Pt. We identified up to three components in each spectrum which are ascribed to elemental Pt(0) and Pt-oxides species, presumably PtO and PtO_2.

For the Pt_5Co/C AM in Fig. 1a, we identified a single component at binding energies, BE = 71.2 eV, ascribed to Pt(0). As expected the AM catalysts submitted to an H_2/N_2 atmosphere at high temperature allow getting metallic Pt [20]. For the Pt_5Co/C EG catalyst in Fig. 1b, we identified two additional components to Pt(0), at 72.3 and 74.3 eV ascribed to PtO and PtO_2 [24]. For the PtCoRu/C MW catalyst in Fig. 1c and for the PtCoRu/C EG catalyst in Fig. 1d, we also identified two additional components to Pt(0), at BE = 73.3 eV and at BE = 75.4 eV. Here it is

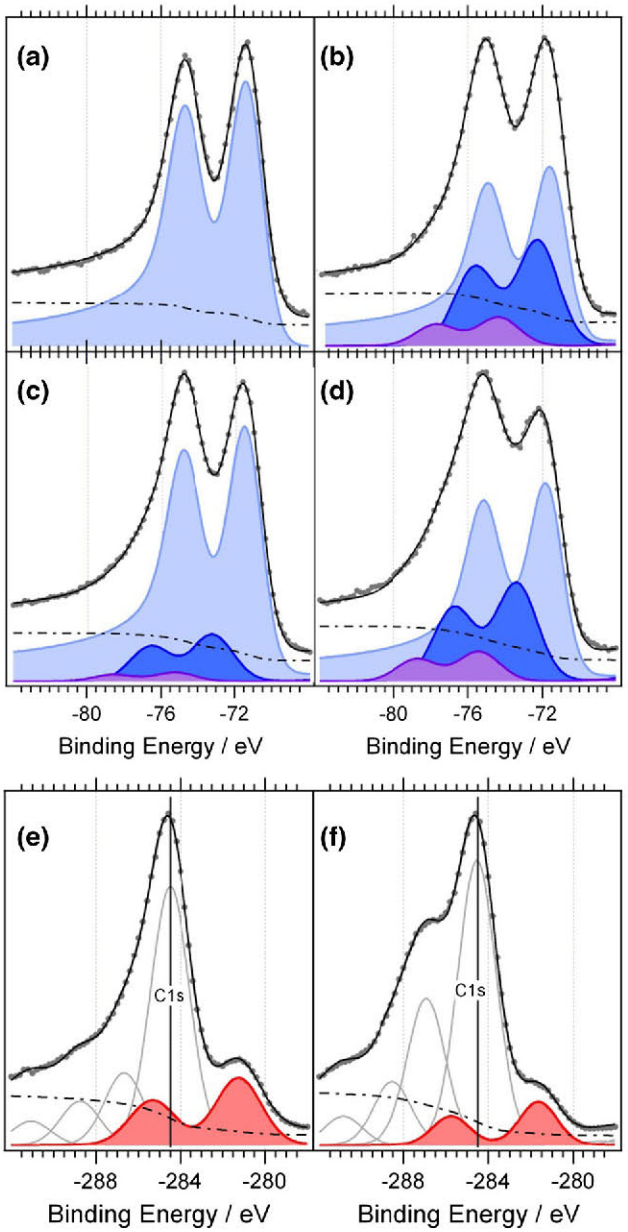

Fig. 1 XPS spectra of Pt 4f from **a** Pt_5Co/C AM **b** Pt_5Co/C EG **c** PtCoRu/C MW **d** PtCoRu/C EG and of Ru 3d from **e** PtCoRu/C MW and **f** PtCoRu/C EG

Table 2 XPS determined percentage (% wt) of metallic Ptand Pt-oxides

Catalyst	Metallic Pt [% wt]	Pt-oxides [% wt]
Pt_5Co/C AM	100	0
$Pt_{10}Co$/C AM	100	0
PtCoRu/C MW	86	14
PtCoRu/C EG	65	35
$Pt_{10}Co$/C EG	66	34
Pt_5Co/C EG	62	38

worth noting that extra components are shifted apart 1 eV to more bounded states in both PtCoRu/C with respect to the nominal values of PtO and PtO_2. This shift has been already reported in the literature [25, 26]. Jung et al. [27] analyzing Pt-oxide thin films in the region of Pt 4f core level have also reported a component at 73.3 eV ascribed to the formation of an intermediate oxide, probably Pt_2O_3-like.

The contribution to the Pt 4f raw spectra of the peaks corresponding to the Pt-oxides is 14 % in the PtCoRu/C synthesized by MW method and in those catalysts obtained by the EG method reached almost 40 % as shown in Table 2.

In regard to Ru, the XPS spectra of PtCoRu/C catalysts were analyzed in the region of the Ru 3d core-level peak, which partially overlaps with the C 1 s core-level peak. Each of these elemental spectra is composed of two identical peaks for Ru, which correspond to the spin–orbit split 3d 5/2 and 3d 3/2 (with relative intensities 3:2), and for C a single peak 1 s, for each component. For PtCoRu/C MW and PtCoRu/C EG the XPS spectra of Ru are shown in Fig. 1e and f respectively. We identified a single component of Ru 3d at BE = 281 eV for the PtCoRu/C MW catalyst, and at BE = 281.5 eV for the PtCoRu/C EG catalyst (the existence of only a single component was also corroborated by measuring the Ru 3p peak, not shown). The Ru 3d peaks for the PtCoRu/C MW catalyst can be assigned to RuO_2 (280.8 eV), and although in the PtCoRu/C EG catalyst it is shifted from the bulk binding energy of RuO_2, it could still be assigned to it due to final state effects because of the small size of NP [28]. This final state effect produces binding energy shifts to more bound states. This core level shifts of small metallic NP over poor conducting substrates comes from the positive charge that remains in the NP once created the electron–hole pair during the photoemission process, as this charge is not neutralized in times relevant to photoemission due to the weak NP-substrate interaction.

Besides the single Ru 3d component, in Fig. 1e and f, several C 1 s components are plotted. The XPS peak deconvolution of C 1 s shows four single peaks, at ca. 284.5 eV, 287 eV, 288.5 eV and 291 eV, which could be assigned according to increasing binding energy values: C=C (284.45 eV) and C–C (285.3 eV) for the signal at 284.5 eV; C–O (286.9 eV) and >C=O (287.2 eV) for the signal at 287 eV; –COO (288.96 eV) for the peak at 288.5 eV; and ester group (292.3 eV) for the peak at 291 eV [29, 30].

The Co 2p XPS spectra (not shown) of the synthesized catalysts exhibit peaks with binding energies that can be assigned to Co (0) (778.3 eV), $Co(OH)_2$ (781 eV), and CO_3O_4 or CoO at (780.3 eV) [24].

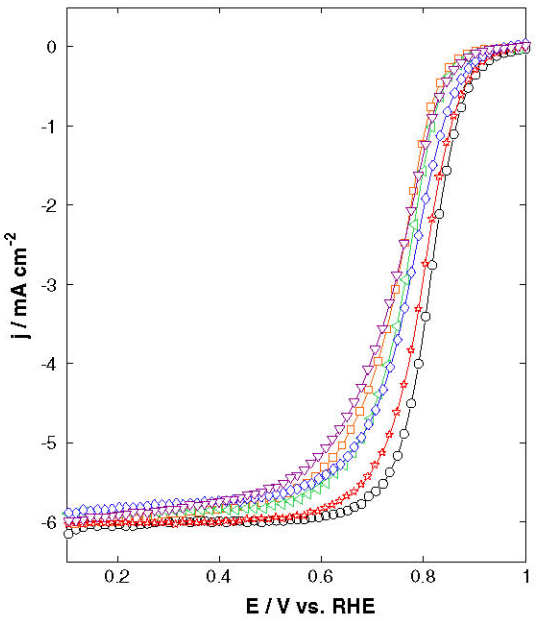

Fig. 2 Polarization curves for ORR in O_2 saturated 0.5 M H_2SO_4 at v = 0.005 Vs ^{1} and ω = 2,000 rpm on $Pt_{10}Co/C$ AM (○), Pt_5Co/C AM (☆), PtCoRu/C MW (◇), Pt_5Co/C EG (▷), $Pt_{10}Co/C$ EG (▽) and PtCoRu/C EG (□) catalysts. (Color figure online)

In all cases the spectra were fitted using a Voigt function for each peak plus a Shirley-type background. The total fitted intensities along with the experimental ones are shown in each spectrum.

3.2 Electrochemical characterization

To assess the activity for ORR we recorded polarizations curves at different rotation rates between 1.0 and 0.2 V scanning the working electrode potential at a rate of 0.005 Vs^{-1} (LSV). The current densities of the polarization curves shown in this work were calculated taking into account the geometric area of the electrode. The background current was measured by running the polarization curves under identical conditions as the LSV for ORR, under N_2-purged 0.5 M H_2SO_4 solution. This background current was subtracted from the experimental ORR current to eliminate any contributions of capacitive current. Typical polarizations curves for ORR on $Pt_{10}Co/C$ AM and EG, Pt_5Co/C AM and EG, PtCoRu/C EG and PtCoRu/C MW electrodes at a rotating disc rate ω = 2,000 rpm are shown in Fig. 2a, b and c, respectively. In order to determine the electrocatalytic activity of each electrode, the current values of the polarization curves for the ORR were used to calculate according to Koutecky- Levich the kinetic current at E = 0.8 V. The specific activity (SA) and mass activity (MA) values of the tested electrode are listed in Table 1. It is notice, that EG catalysts exhibit lower MA and ECSA values than those of AM and MW catalysts. The reason of this behavior can be the smaller amount of metallic Pt in EG catalysts. Further investigation would be necessary to fully understand these results. The onset potential, at which the current for oxygen reduction is first observed, was determined by the point of intersection of two lines, one drawn extending the baseline (i.e. from 1 to 0.9 V) and the other extending the increasing linear portion of ORR curve, the onset potential for each catalysts is shown in Table 1. The superposition of the ORR polarization curves confirmed that the catalysts exposed to a reducing atmosphere, AM catalysts, alongside with MW catalyst have the highest onset potential for the ORR, due to the same reason written right above, i.e. the smaller amount of metallic Pt in EG catalysts.

To find out how the composition and the synthesis method of the electrode materials influence the methanol tolerance, we measured the polarization curves in O_2 saturated 0.5 M H_2SO_4 + 0.1 M CH_3OH at ω = 2,000 rpm with the different catalysts. We show in Fig. 3a the polarization curves for the ORR employing $Pt_{10}Co/C$ EG and AM and in Fig. 3b those on Pt_5Co/C EG and AM. It is clear from the figures that the AM catalysts show less methanol tolerance [31] and that the amount of Co has also an influence on methanol tolerance, i.e. higher Co amount diminishes the MOR [32]. From the electrocatalytic behavior of the tested electrodes, we conclude that the best catalyst for ORR is not the most tolerant to methanol presence. Polarization curves for the ORR on PtCoRu/C EG and PtCoRu/C MW, which are shown in Fig. 3c, exhibit a remarkable high methanol tolerance. It seems that the presence of Ru in the catalyst has contributed to increase the alcohol tolerance, XPS results identify a unique species RuO_2, which has been found to be less active for methanol oxidation [33, 34].

It is important to point out that the requirements demanded for a suitable cathode catalyst are: (i) good catalytic behavior for the ORR and (ii) high tolerance to methanol presence. Therefore, not only the synthesis method but the composition of the catalysts are important in order to obtain a suitable cathode catalyst. In Fig. 4a, for $Pt_{10}Co/C$ EG, and in Fig. 4b, for PtCoRu/C EG the polarization curves for ORR in the presence of different amount of methanol are shown. Notice that $Pt_{10}Co/C$ EG, despite being obtained by the same method that PtCoRu/C EG, shows that higher concentrations of methanol makes it less resistant. To confirm these results, the following investigation on the electrocatalytic behavior of PtCoRu/C and PtCo/C catalysts for methanol oxidation, in a N_2 saturated 0.1 M CH_3OH + 0.5 M H_2SO_4 solution, was carried out by cyclic voltammetry. In Fig. 5 are shown the current density-potential profiles on $Pt_{10}Co/C$ AM and PtCoRu/C EG, the current densities are given on the basis

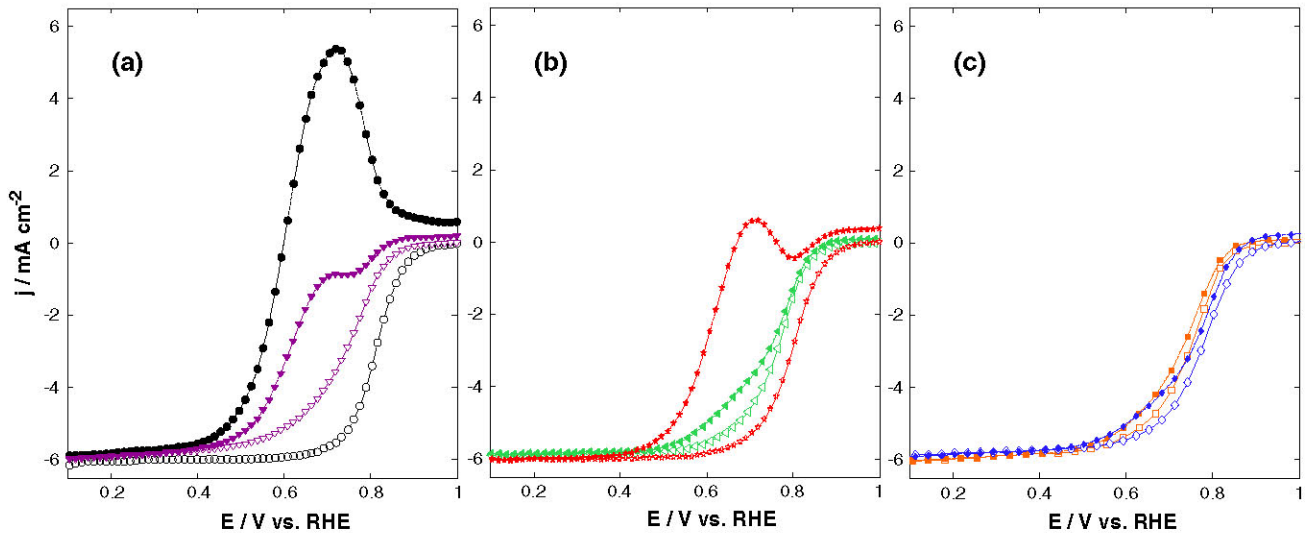

Fig. 3 Polarization curves for ORR in O_2 saturated 0.5 M H_2SO_4 at $v = 0.005$ Vs $^{-1}$ and $\omega = 2{,}000$ rpm without and with 0.1 M CH_3OH **a** on $Pt_{10}Co/C$ AM without CH_3OH (○) or with 0.1 M CH_3OH (●) and on $Pt_{10}Co/C$ EG without CH_3OH (▽) or with 0.1 M CH_3OH (▼), **b** on Pt_5Co/C EG without CH_3OH (▷) with 0.1 M CH_3OH (▶) and on Pt_5Co/C AM without CH_3OH (☆) or with 0.1 M CH_3OH (★) and **c** PtCoRu/C EG without CH_3OH (□) or with 0.1 M CH_3OH (■) and on PtCoRu/C MW without CH_3OH (◇) or with 0.1 M CH_3OH (◆). (Color figure online)

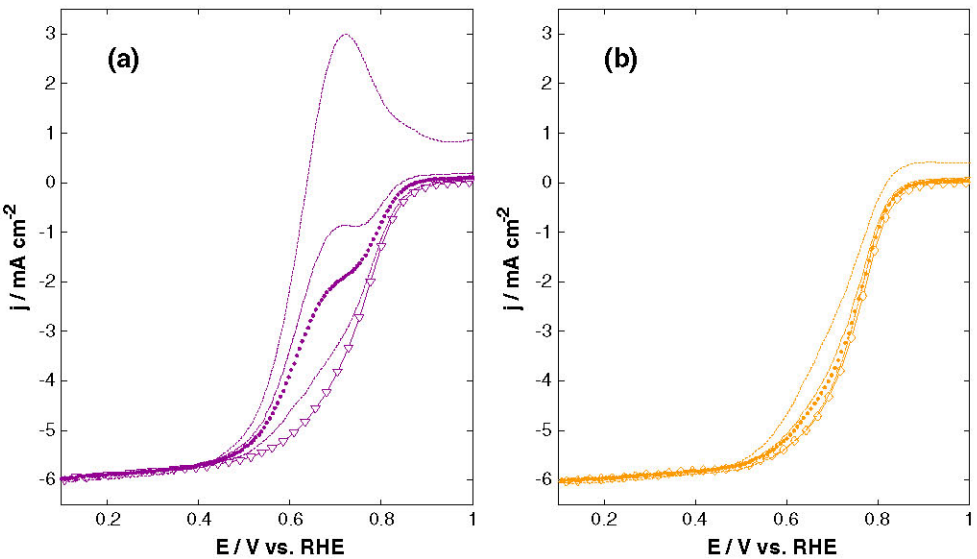

Fig. 4 Polarization curves for ORR in O_2 saturated 0.5 M H_2SO_4 with different CH_3OH concentrations at $v = 0.005$ Vs $^{-1}$ and $\omega = 2{,}000$ rpm **a** on $Pt_{10}Co/C$ EG without CH_3OH (▽), with 0.01 M CH_3OH (— • —), with 0.05 M CH_3OH (•), with 0.1 M CH_3OH (— —), with 0.5 M CH_3OH (- -) and **b** on PtCoRu/C EG without CH_3OH (□), with 0.01 M CH_3OH (— • —), with 0.05 M CH_3OH (•), with 0.1 M CH_3OH (— —), with 0.5 M CH_3OH (- -). (Color figure online)

of the electrochemically active area. It can be seen that in the increasing potential scan (forward scan), the onset potential for methanol oxidation on PtCoRu/C EG has almost the same value as the one on $Pt_{10}Co/C$ AM (onset potential ca. 0.36 V). In the decreasing potential scan (backward scan) the methanol oxidation peak emerges immediately after the surface oxide reduction happens. In particular, for the PtCoRu/C EG catalyst, the methanol oxidation peak in the reverse scan is located at lower potential value, i.e. 0.50 V, in comparison to 0.65 V for $Pt_{10}Co/C$, indicating a lower electrocatalytic reactivity of the PtCoRu/C EG catalyst for this alcohol oxidation. From this analysis we conclude that PtCoRu/C EG is not a suitable catalyst for methanol oxidation.

Taking into account the curves shown in Fig. 3, we define the term relative methanol tolerance percentage (RMT %) of the prepared catalysts, considering the ratio of the difference between the current density for ORR with and without methanol at 0.7 V for any catalyst and the same difference on the catalysts with the highest activity for MOR (i.e. $Pt_{10}Co/C$), the calculated ratio for each catalyst is then subtracted from 1 and multiplied by 100.

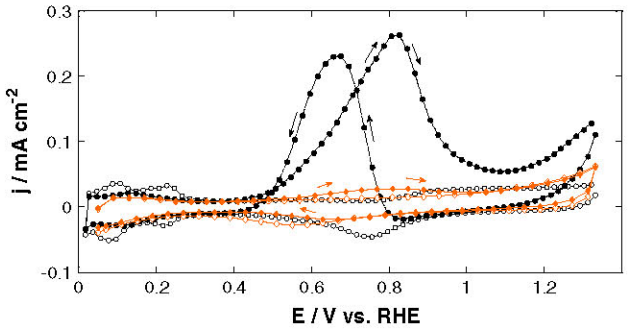

Fig. 5 Cyclic voltammograms for MOR in N_2 purged 0.5 M H_2SO_4 at v = 0.010 Vs $^{-1}$ and ω = 2,000 rpm on $Pt_{10}Co$/C AM without CH_3OH (○) or with 0.5 M CH_3OH (●) and on PtCoRu/C EG without CH_3OH (□) or with 0.5 M CH_3OH (■). (Color figure online)

Table 3 Relative methanol tolerance percentage (RMT %)of the prepared catalysts

Catalyst	RMT %[a]
$Pt_{10}Co$/CAM	0
Pt_5Co/CAM	54.68
$Pt_{10}Co$/CEG	71.78
Pt_5Co/CEG	92.14
PtCoRu/C EG	94.88
PtCoRu/C MW	95.98

[a] At 0.7 V in O_2 saturated 0.5 M H_2SO_4 + 0.1 M CH_3OH

The RMT % of all catalysts are listed in Table 3. Notice that the highest RMT % values correspond to PtCoRu/C catalysts and the lowest value to PtCo/C AM catalysts.

4 Conclusions

- The AM and MW methods allow to get the best catalysts for ORR.
- The AM method used to obtain suitable catalysts for ORR worsens methanol resistance, in contrast to the EG method.
- A higher Co amount in the catalyst composition diminishes methanol oxidation.
- A strong effect on the methanol tolerance is achieved by the addition of Ru in the catalyst composition.

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