

ON THE PREPARATION AND STABILITY OF BIMETALLIC PtMO/C ANODES FOR PROTON-EXCHANGE MEMBRANE FUEL CELLS

N.P. Lebedeva

G.J.M. Janssen

To be submitted to *Electrochimica Acta*

Acknowledgement/Preface

The authors would like to thank Ing. D. Borger (ECN, Petten) for ICP-AES measurements and Ing. M.W.G.M. Verhoeven (Eindhoven University of Technology, Eindhoven) for XPS analysis of PtMo/C samples.

Abstract

Synthesis of the bimetallic carbon supported PtMo electrocatalysts via the reductive co-precipitation with either formaldehyde or formic acid as reducing agent is presented. The materials synthesized were characterised with respect to their bulk and surface composition using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray photoelectron spectroscopy (XPS). The electrochemical behaviour of the materials was characterised with the help of cyclic voltammetry in sulfuric acid solutions as well as in membrane-electrode assemblies (MEAs). The stability of the electrocatalysts was also investigated. Our experimental results also show that bimetallic PtMo/C catalysts are apparently inherently unstable and suffer from the gradual loss of Mo due to its dissolution into the electrolyte, regardless of whether the components are well-mixed or present in the segregated phases.

CONTENTS

INTRODUCTION	4
EXPERIMENTAL	6
PtMo/C catalyst preparation	6
Characterisation of PtMo/C catalysts	7
Preparation of the PtMo/C electrodes and membrane-electrode assemblies (MEAs).	7
Electrochemical testing of the PtMo/C electrodes and membrane-electrode assemblies (MEAs)	7
RESULTS AND DISCUSSION	9
Preparation and characterisation of the PtMo/C catalysts	9
Electrochemical characterisation of the PtMo/C catalysts	10
Stability of the PtMo/C catalysts	12
CONCLUSIONS	15
TABLES	17
SCHEMES	18
FIGURES	19
REFERENCES	31

INTRODUCTION

Bimetallic PtMo catalysts have long been recognised for their excellent catalytic activity in the oxidation of small organic molecules such as carbon monoxide [1-18], methanol [4,15,19,20] and formaldehyde [19]. These special properties made PtMo materials attractive for the use as CO- and reformato-tolerant anode catalysts in the proton-exchange membrane fuel cells [3,5-10,12,15-18,21]. A wide range of the bimetallic PtMo materials has been prepared and studied: single crystals of the true PtMo alloys [1,2,4], carbon supported PtMo catalysts [3,5-10,13-18,21] and various Pt electrodes, whose surface has been modified with Mo species [3,11,12,19].

The mechanism of the CO tolerance of PtMo catalysts has been extensively discussed in the literature. Studies of the CO oxidation on the PtMo alloy single crystals indicated that the conventional bifunctional mechanism is responsible for the CO tolerance of these materials, where the adsorption of CO occurs only on Pt sites and oxygen-containing species is generated on the Mo sites [1,2,4]. Recent works of the group of Ticianelli on the CO and reformato tolerance of the PtMo catalysts, prepared via the so-called formic acid route, showed that the behaviour of these materials can also be described reasonably well with the classic bifunctional mechanism [15,18]. It is important to realize, however, that since the formic acid route does not apparently involve any heat treatment step, no real alloying of the components can be expected. This also seems to be true for the bimetallic PtMo catalysts synthesized following the colloidal Bönemann route [3,22,23]. It appears, therefore, that similarly to the case of the PtRu catalysts [24-26], real alloying of the catalyst components is not a necessary pre-requisite for a good CO and reformato tolerance of the catalyst and just intimate mixing of Pt and Mo would suffice. Although Mo-modified Pt materials also exhibit some activity in the oxidation of small organic molecules [3,11,12,19], their performance was shown to be inferior to that of the PtMo/C materials with well-mixed components [3,12]. It appears, therefore, that in order to achieve the highest activity bimetallic PtMo catalysts should be either truly alloyed or have the components mixed on the atomic scale.

It is reasonable to expect that the structure and, hence, the electrochemical activity and stability of the catalyst would strongly depend on the synthesis route and its parameters. A detailed characterisation of the products is therefore essential in order to select the best preparation procedure for the bimetallic catalysts and to understand their electrochemical behaviour.

In this work we present a comparison of the two synthesis routes for the preparation of carbon supported bimetallic PtMo catalysts – the so-called formic acid route, developed by the group of Ticianelli [15,18,27], and a modified version of the formaldehyde route, previously employed for the preparation of PtRu catalysts [25]. Physical characterisation of the surface and bulk composition of the products allowed us to link their structure and homogeneity to the electrochemical performance and stability of these catalysts.

EXPERIMENTAL

PtMo/C catalyst preparation

Two different methods were used to prepare bimetallic PtMo/C catalysts. Method I employed the reduction of the Pt and Mo precursors with formaldehyde in the presence of a suspension of carbon support similarly to the procedure described in the patent of Degussa AG [25]. Method II involved the reduction of Pt and Mo precursors with formic acid in the presence of carbon support suspension according to the procedure described by the group of Ticianelli [15,18,27].

To prepare a PtMo catalyst with Pt:Mo ratio of 6:4 and the total metal loading of 20 w% according to Method I, the appropriate amounts of Pt(NO₃)₂ solution (30% Pt, Merck) and MoCl₅ (99.9+%, Aldrich) were added to a vigorously stirred aqueous slurry of Vulcan XC-72. The mixture was subsequently heated to 80°C and an aliquot of formaldehyde (37% solution, pro analysi, Merck) that corresponded to the 5-times excess of the stoichiometric amount required for complete reduction of both Pt and Mo was added. Synthesis was performed at two different values of final pH: 0.9 and 2.5. In the latter case pH of the solution was adjusted with a 15 % solution of KOH. The slurry was stirred further for about 16 hours at room temperature, filtered, washed on the filter with water and dried at 80°C under a nitrogen flow for at least 2 hours.

Carbon supported PtMo catalysts with the same Pt/Mo ratio and total metal loading were also prepared following Method II. Formic acid (pro analysi, Merck) was added in 5-times excess of the stoichiometric amount necessary to reduce both Pt and Mo to vigorously stirred aqueous slurry of Vulcan XC-72. The slurry was heated to 50°C. The stoichiometric amounts of H₂PtCl₆ (40% Pt, for synthesis, Merck) and (NH₄)₆Mo₇O₂₄·4H₂O (extra pure, Merck) were dissolved in a minimum amount of water and these solutions were slowly dropwise added to the Vulcan XC-72 slurry. The progress of the reduction of H₂PtCl₆ in the slurry was periodically checked with saturated KI solution [27]. If unreacted Pt-species were detected, the addition of the Pt and Mo precursors was stopped till the reduction of H₂PtCl₆ was complete and then resumed again. Then the slurry was stirred further for about 16 hours at room temperature, filtered, washed on the filter with water and dried at 80°C under a nitrogen flow for at least 2 hours. Mo/C catalyst was also prepared according to the Method II.

Characterisation of PtMo/C catalysts

The elemental composition of the prepared PtMo/C catalysts was verified with the help of inductively-coupled plasma atomic emission spectroscopy (ICP-AES). Analysis was performed using Varian Vista axial plasma spectrometer. The surface composition of as-prepared catalysts was investigated using X-ray photoelectron spectroscopy (XPS). The XPS measurements were done with a VG CLAM 2 hemispherical electron energy analyser with single channeltron detection and a VG XR3 twin anode (Al/Mg) X-ray source. Spectra were obtained with the aluminium anode ($AlK_{\alpha}=1486.6$ eV) used at the power of 250 W with constant pass energy of 50 eV. Background pressure of the vacuum system was ca. $2 \cdot 10^{-9}$ mbar. Samples were prepared by pressing a small amount of the catalyst powder into In foils.

Preparation of the PtMo/C electrodes and membrane-electrode assemblies (MEAs)

For testing of the electrochemical performance of the synthesised materials, catalytic inks were prepared as follows: an aliquot of propanol-1 (pro analysi, Merck) and of 5 w.% solution of Nafion (EW 1100, DuPont) were added to a certain amount of PtMo/C catalyst so that the resulting ink would have 1.3 w.% content of total metal and 2 w.% of Nafion. The slurry was dispersed using a T25 B homogeniser (IKA Labortechnik, Germany) at 24000 rpm for a few minutes.

Two types of the electrodes were made using the catalytic inks. For the electrochemical tests in a standard three-electrode cell with liquid electrolyte the PtMo/C inks were applied on a smooth Pt electrode and dried at 130°C under the flow of nitrogen for 30 minutes. Fabrication of the anode for the tests in a membrane-electrode assembly (MEA) involved application of a certain amount of PtMo/C ink on a SGL 31 BC carbon backing material (SGL Carbon) to give a final loading of 0.4 mg of total metal per cm^2 of the backing. The composite was first dried at room temperature and then at 130°C under the flow of nitrogen for 30 minutes. Cathode for MEA testing was prepared in a similar way to the anode, except that it contained only Pt/C instead of PtMo/C. Nafion 112 (DuPont) was used as electrolyte. MEAs were hot-pressed at 130°C and 4 bars for 90 s.

Electrochemical testing of the PtMo/C electrodes and membrane-electrode assemblies (MEAs)

A standard three-electrode electrochemical cell was used for the testing of PtMo/C electrodes in sulfuric acid electrolytes. Platinised platinum was used as a counter electrode and reversible

hydrogen electrode as a reference electrode. 0.5 M and 0.1 M solutions of H₂SO₄ were prepared from concentrated H₂SO₄ (pro analysi, Merck) and high purity MilliQ (Millipore) water. The solutions were deoxygenated prior to each experiment.

MEAs were tested in a fuel cell test station at room temperature. For recording cyclic voltammograms of a MEA hydrogen was supplied to the cathode (70 ml/min) so that the cathode serves both as a counter electrode as well as a reference electrode, while the anode was continuously purged with nitrogen (70 ml/min).

All electrochemical experiments were performed using a computer-controlled Autolab PGSTAT 20 potentiostat.

RESULTS AND DISCUSSION

Preparation and characterisation of the PtMo/C catalysts

The results of the elemental analysis of the bulk and surface composition of the synthesized PtMo/C catalysts are summarized in Table 1. The XPS spectra of the two analysed PtMo/C samples for Mo 3d and Pt 4f regions are shown in Figs. 1a and 1b, respectively.

As can be seen from Table 1 the bulk composition of the catalysts is relatively close to the target, although some loss of Mo in the synthesis is evident. XPS peaks at 235.6 and 232.4 eV indicate that Mo is present in the catalysts in the form of its trioxide, MoO₃ [28]. In the Pt 4f region of the XPS spectra two peaks at 71.1 and 74.4 eV are observed (see Fig. 1b), which are characteristic to metallic Pt [28]. The latter finding appears somewhat surprising given the well-known fact that the Pt nano-particles are often covered with the surface oxide layer. Reduction of the surface Pt oxide under the XPS measurement conditions can be one of the possible explanations for this observation [29].

XPS analysis also shows that the surface composition of the PtMo/C catalysts differs noticeably from that of the bulk. There is significant enrichment of the surface with Mo, especially for the catalyst prepared via the formaldehyde route (Table 1).

These effects – some loss of Mo in the catalyst preparation and enrichment of the catalysts surface with Mo – can be rationalised considering the inorganic chemistry of aqueous Mo species [30]. It is well-known that it is the Mo⁶⁺ species that is the most stable in aqueous solutions in the presence of oxygen [30]. Its reduction to lower oxidation states, but never to metallic Mo, takes place only in the presence of strong reducing agents such as hydrogen or Sn²⁺ [30]. Moreover, Mo⁶⁺ species exists in different forms depending on the pH of the solution (see Scheme 1), all of them, except hydrated MoO₃, being water-soluble [30].

Taking this into account it can be concluded that synthesis of PtMo/C catalysts has to be performed in a narrow pH window between ca. 0 and 2 to avoid a dramatic loss of Mo. Even if this condition is fulfilled some Mo loss would still occur as only *partial precipitation* of Mo in the form of MoO₃·xH₂O takes place [30]. This explains why the composition of all prepared PtMo/C catalysts differs slightly from the target. It is still unclear though why the deviation from the target is higher for the catalyst prepared via the formic acid route as the final pH of the

solution was kept at 0.9 for both formaldehyde and formic acid routes. The same deviation of the bulk composition of the catalysts prepared using formic acid was observed in the previous work by Santiago et al. [15], who obtained Pt_{0.72}Mo_{0.28}/C catalyst instead of a targeted Pt_{0.6}Mo_{0.4}/C. As the syntheses were performed in air, no reduction of either Mo⁶⁺ or Mo⁵⁺ precursor is expected to take place as confirmed by XPS data.

To explain the variation of the degree of the surface enrichment with Mo, one has to consider the kinetics of the Pt reduction and that of the precipitation of MoO₃·xH₂O. From our experiments it was clear that the reduction of the Pt precursor occurred quickly when formaldehyde was used, while reduction with formic acid took much longer. Precipitation of MoO₃·xH₂O is known to be a relatively slow process [30]. Hence, there is a significant mismatch of the rates of the Pt precursor reduction and that of the precipitation of MoO₃·xH₂O when formaldehyde is used in the synthesis. As a result a strongly inhomogeneous catalyst is produced, apparently with a sort of a core-shell structure, where the component that precipitates first - Pt in our case - is in the core of a particle and the “slower” component – Mo - is at the surface. In case of Method II that makes use of formic acid, the disbalance of the Pt precursor reduction rate and that of the Mo precursor precipitation seems to be reduced enabling synthesis of a more homogeneous PtMo/C catalyst (see Table 1).

Electrochemical characterisation of the PtMo/C catalysts

The cyclic voltammograms of the PtMo/C and Mo/C catalysts in 0.1 M and 0.5 M H₂SO₄ are shown in Figures 2 and 3, respectively. Figure 4 shows the voltammograms of the PtMo/C catalysts in MEA arrangement. For PtMo/C electrodes two main peaks at ca. 0.45 and 0.65 V are observed on a positive-going scan. Their ratio for PtMo/C varies depending on the preparation method. The peak at ca. 0.65 V is much more intense for the catalysts A, while it is clearly less pronounced for the catalysts B and C (see Figs. 2 and 3). Mo/C exhibits only one main peak at ca. 0.65 V on the positive-going scan. In the potential region below ca. 0.35 V a number of less defined peaks are visible for all catalysts investigated. For all PtMo/C catalysts as well as for Mo/C two poorly resolved peaks are visible on the negative-going scan in the potential region between ca. 0.4 and 0.2 V. While the cyclic voltammograms of the PtMo/C as well as Mo/C electrodes in 0.1 M and 0.5 M sulfuric acid are practically identical, the profiles of the PtMo/C electrodes in MEA arrangement generally exhibit much less defined voltammetric features. Most likely, this phenomenon is specific to the operation of the MEA setup (higher ohmic drop, non-negligible presence of the contaminants in the system) and does not signify any change of the characteristics of the catalyst itself.

Earlier studies on well-defined PtMo alloy single crystals [1,2,4] show that the cyclic voltammograms of these alloys are complex and in most of the cases only tentative ascription of the peaks is possible allowing qualitative distinction between red-ox response of Pt and that of Mo. Thus, it is generally accepted that the peak at ca. 0.45 V on the positive-going scan and its negative-going scan counter parts at 0.4-0.2 V represent the red-ox transformations of Mo. Current below ca. 0.35 V originates from the overlap of the electrochemical activity of Pt with that of Mo [1,2,4]. From the comparison of the electrochemical response of a Mo single crystal to that of a PtMo alloy combined with an ex situ XPS study of the surface species of PtMo alloy single crystal, it has been suggested that Mo is present in the oxidised form in the entire potential window, changing from Mo^{3+} to Mo^{6+} as the potential increases [1,2,4].

As has been shown in a number of previous publications, cyclic voltammograms of the ETEK PtMo/C catalysts [5-7,9,14,17] as well as the PtMo/C catalysts prepared following Method II [15,18] exhibit basically the same voltammetric features as PtMo alloys. In situ EXAFS studies of an ETEK PtMo/C catalyst showed that Pt and Mo were alloyed [6]. In situ XANES and XAS studies of the surface species of these catalysts confirmed earlier reported data on surface chemistry of PtMo single crystals and showed that Mo is oxidised at all potentials and is present as Mo^{4+} even at the potentials close to 0 V [6,7]. It has been proposed in the later work of the Mukerjee et al. that Mo is present in Mo^{5+} oxidation state at the potentials between 0 and 0.24 V and then oxidises further to Mo^{6+} as the potential increases to ca. 0.54 V [9]. Unfortunately, no detailed information on the surface composition and its dependence on potential was reported for the PtMo/C catalysts prepared via Method II. Similarity of the cyclic voltammograms of these catalysts to the voltammetric patterns of the PtMo/C materials from ETEK suggests though that they might be essentially the same, although it is difficult to assess the degree of the components alloying.

Our voltammetric results agree well with the previously reported data [1,2,4-7,9,14,15], except that an extra peak at ca. 0.65 V is observed for all PtMo/C electrodes. The origin of this peak can be inferred when the cyclic voltammogram of Mo/C catalyst is considered (see. Figs. 2d and 3d). In agreement with earlier studies [15,18] the Mo/C voltammogram exhibits a major peak at ca. 0.6 V, indicating that non-alloyed carbon supported Mo undergoes a red-ox reaction in this potential region. This suggests that for all catalysts investigated in the present work some pure non-alloyed Mo – most likely $\text{MoO}_3 \cdot x\text{H}_2\text{O}$ - is present on the surface of carbon along with mixed Pt-Mo phase. The amount of this segregated Mo varies depending on the preparation procedure and is apparently the highest for the catalyst A and the lowest in the case of catalyst C. As explained in the previous section, the preparation procedure strongly influences the

homogeneity and, hence, the surface composition of the catalyst. This, in turn, is reflected by the shape of the cyclic voltammogram. In this sense cyclic voltammetry in the supporting electrolyte can be used as a sensitive tool to assess the homogeneity of the PtMo/C catalysts.

Stability of the PtMo/C catalysts

The evolution of the voltammetric profiles of the PtMo/C electrodes upon cycling in 0.1 M and 0.5 M H₂SO₄ as well as in MEA arrangement is shown in Figures 5, 6 and 7. In all cases a gradual decrease of the peaks, related to the red-ox reactions of Mo, is evident, suggesting that Mo dissolves into the electrolyte. Quantitative differences in the rate of the Mo dissolution from the PtMo/C catalysts in various electrolytes become apparent from the comparison of the Figures 5,6 and 7 and will be discussed later on in detail.

The fact of Mo dissolution has been confirmed in a test with a smooth Pt electrode immersed into the working electrolyte (either 0.1 M or 0.5 M H₂SO₄ solution). Figure 8 shows that a peak at ca. 0.45 V, very characteristic to the presence of Mo species in the system, appears on the cyclic voltammogram of the Pt test electrode after a few cycles of the working electrode. The dissolution of Mo from the surface of the PtMo/C catalysts in the MEA arrangement was confirmed by recording a cyclic voltammogram of a Pt counter electrode after a few cycles of the working electrode. Again, a peak at ca. 0.45 V characteristic to the presence of Mo species appeared (see Fig. 9), indicating that Mo dissolves from the working PtMo/C electrode and diffuses through the Nafion membrane to the counter electrode.

In an attempt to quantify the stability of the synthesized PtMo/C materials we plotted the peak current for both voltammetric peaks – at ca. 0.45 and 0.65 V - versus the number of cycles. An example of such dependence for the evolution of the profile of the catalyst C is shown in Figure 10. The experimental results can be fitted with a power function, which exponent value can be used to compare the rates of dissolution of different PtMo/C materials at least qualitatively. The exponents for the degradation due to the loss of Mo for all electrodes in 0.1 M and 0.5 M H₂SO₄ as well as in MEA are summarised in Figure 11. Our results indicate that the highest rate of dissolution for all materials is in 0.5 M H₂SO₄, while MEAs show the lowest rate of Mo loss. The other trend is that in a given electrolyte catalyst A shows much higher Mo dissolution rates than the other catalysts.

The poor stability of all PtMo/C electrodes in 0.5 M H₂SO₄ is directly related to the amphoteric character of MoO₃, which readily dissolves at pH below 0 [30]. In 0.1 M H₂SO₄ MoO₃ should

be stable [30] and the most likely reason for Mo loss can be the formation of a soluble product in the electrochemical reduction of MoO_3 at low potentials. The acidity of Nafion is known to be very high and this in principle should promote the dissolution of MoO_3 . We speculate that immobility of the counter anions of Nafion and a slow transport of the dissolution product away from the electrode surface might lead to a decreased rate of Mo loss under our experimental conditions. It cannot be excluded, however, that the rate of Mo dissolution from the PtMo/C would increase under the operation conditions of a real fuel cell.

Different dissolution rates of the PtMo/C electrodes in a given electrolyte can be related to their homogeneity. As can be seen from our results (Figs. 5 and 6) in most of the cases the peak at ca. 0.65 V decreases quicker than that at ca. 0.45 V, suggesting that the non-alloyed MoO_3 phase dissolves more rapidly than Mo from the mixed Pt-MoO₃ phase. Therefore, the stability of a given electrode material is directly related to the degree of mixing of the components and, hence, strongly depends on the preparation method. A more homogeneous catalyst C usually shows much lower Mo loss than a heterogeneous catalyst A (Figs. 5,6 and 7).

The stability of PtMo/C catalysts is still a point of controversy in the existing literature. While the dissolution onset for pure Mo is reported to be at ca. 0.4 V [4 and references therein], research on PtMo alloy single crystals showed that $\text{Pt}_{0.75}\text{Mo}_{0.25}$ and $\text{Pt}_{0.70}\text{Mo}_{0.30}$ alloys are stable at the potentials between 0 and 0.8 V in 0.5 M H_2SO_4 and do not exhibit any loss of Mo upon repeated cycling in this potential window [1,2]. Much inhibited dissolution of Mo from the PtMo alloys was attributed to the stabilisation effect of the alloy with Pt [4].

ETEK PtMo/C catalysts were also reported to be stable upon cycling between 0.05 and 1.2 V in 0.5 M H_2SO_4 for at least 50 consecutive cycles [6,7]. In a later paper Mukerjee et al. report the experimental routine for in situ EXAFS measurements in 0.1 M HClO_4 , where they specifically state that a PtMo/C electrode has been cycled between 0 and 0.65 V, the low 0.65 V upper voltage cutoff being used to avoid any possible dissolution of Mo from the electrode surface [9,14,17]. However, later in the text of the same papers the authors state that the PtMo/C electrode was stable and did not show any Mo loss upon cycling between 0 and 1.2 V in 0.1 M HClO_4 [9,14,17]. Long-term stability of the PtMo/C catalysts from ETEK was also evaluated in [17]. Under steady-state conditions of a fuel cell with cell voltage of 0.6 V and CO content of 100 ppm PtMo/C catalyst from ETEK showed no performance degradation in 1500 hours of operation [17].

Stability of PtMo/C catalysts at potentials as high as 1.2 V appears questionable to us as it is well known that carbon supported metal nanocatalysts degrade due to the (electro)catalytic

corrosion of the carbon support at the potentials above 0.8 V that results in the mechanical loss of metal particles [31]. Another well known degradation mechanism for carbon supported metal electrocatalysts is “sintering” of metal particles during the operation of the electrode, which has been observed and documented even for pure Pt nanoparticles [31].

Less information is available on the stability of the PtMo/C materials prepared via the formic acid route. A decrease of the electrocatalytic activity of PtMo/C prepared according to Method II during the operation of a fuel cell was observed in Ref.15. Mo dissolution was named as one of the possible reasons for the performance loss [15]. Our results seem to confirm this supposition as leaching of Mo species from the catalyst C has been observed even in the MEA arrangement (see Figs. 7, 9, 11).

CONCLUSIONS

Synthesis of the bimetallic carbon supported PtMo electrocatalysts via the reductive coprecipitation with either formaldehyde or formic acid as reducing agent is presented. The materials synthesized were characterised with respect to their bulk and surface composition using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray photoelectron spectroscopy (XPS), respectively. The electrochemical behaviour of the materials was characterised with the help of cyclic voltammetry in sulfuric acid solutions as well as in membrane-electrode assemblies (MEAs). Stability of the electrocatalysts was also investigated.

Elemental analysis of the synthesized materials showed that the bulk composition of the prepared PtMo/C catalysts is close to the target Pt_{0.6}Mo_{0.4}/C. X-ray photoelectron spectroscopy showed that Mo in as-prepared materials is present in the form of its trioxide, MoO₃, while Pt is fully reduced to Pt⁰. A significant enrichment of the surface with Mo, especially for the catalysts prepared via the formaldehyde route, was detected by XPS. Characterisation of the PtMo/C and Mo/C electrocatalysts with cyclic voltammetry suggested the presence of some pure non-alloyed Mo – most likely in the form of MoO₃·xH₂O – on the surface of carbon support along with the mixed PtMo phase. The amount of the segregated Mo-containing phase varies depending on the preparation method and is apparently the lowest for the catalysts prepared via the formic acid route.

The mismatch of the rates of Pt precursor reduction and that of hydrated MoO₃ precipitation is likely to be the reason for the inhomogeneity of the prepared materials. By choosing a proper reducing agent, for example, formic acid, the rates of the two processes can be better matched enabling a better mixing of the components and, hence, synthesis of a more homogeneous catalyst.

The evolution of the voltammetric profiles of the PtMo/C electrodes upon cycling in 0.1 M and 0.5 M H₂SO₄ as well as in the MEA arrangement indicated that Mo dissolves into the electrolyte as a gradual decrease of the peaks, related to the red-ox reactions of Mo, was evident in all cases. It has been shown that in the MEA Mo dissolved from the surface of the anode diffuses through the Nafion membrane to the cathode. The stability of the PtMo/C materials follows two clear trends: (i) the highest rate of the Mo dissolution for all materials was observed in 0.5 M H₂SO₄ and the lowest – in MEA arrangement; (ii) in a given electrolyte, the rate of the degradation of the PtMo/C materials due to the loss of Mo is shown to depend on the

homogeneity and, hence, on the preparation method of the electrocatalysts. The least homogeneous PtMo/C materials in general exhibit the highest rate of Mo loss.

Our experimental results also show that bimetallic PtMo/C catalysts are apparently inherently unstable and suffer from the gradual loss of Mo due to its dissolution into the electrolyte, regardless of whether the components are well-mixed or present in the segregated phases. In the latter case dissolution of Mo occurs at the increased rate.

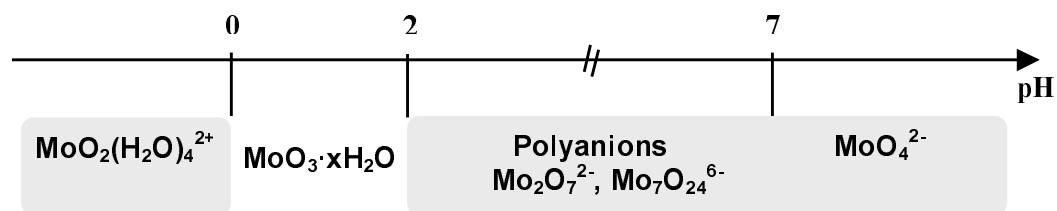
TABLES

Table 1. Elemental bulk and surface composition of the prepared PtMo/C catalysts.

	Method I		Method II
Reducing agent	Formaldehyde		Formic acid
Catalyst acronym	A	B	C
pH	0.9	2.5	0.9
Target composition	Pt _{0.60} Mo _{0.40}	Pt _{0.60} Mo _{0.40}	Pt _{0.60} Mo _{0.40}
Bulk composition (ICP-AES)	Pt _{0.65} Mo _{0.35}	Pt _{0.66} Mo _{0.34}	Pt _{0.73} Mo _{0.27}
Surface composition (XPS)	Pt _{0.14} Mo _{0.86}	-----	Pt _{0.40} Mo _{0.60}

SCHEMES

Scheme 1. Chemistry of aqueous Mo^{6+} species as a function of solution pH [28].



FIGURES

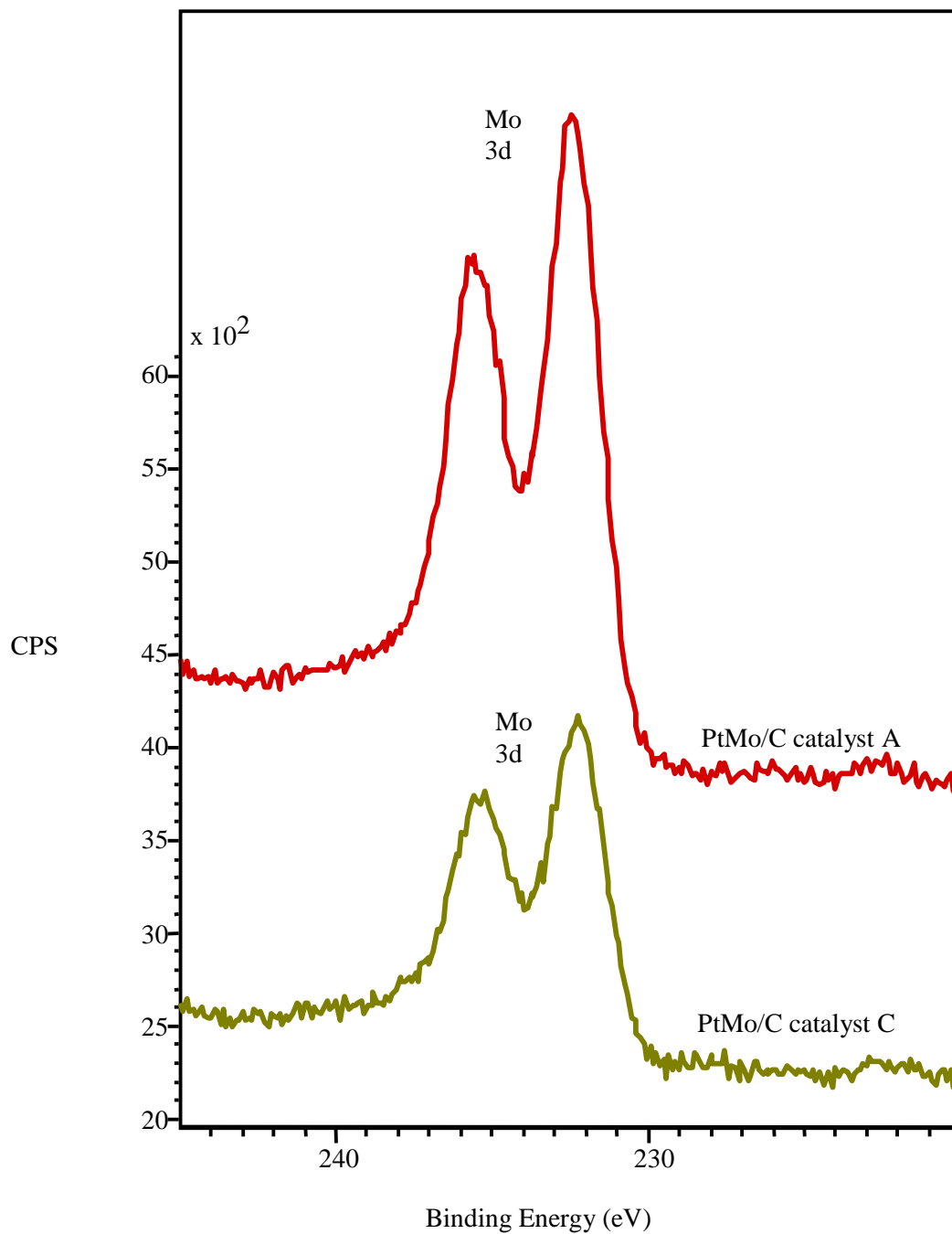


Figure 1a. Mo 3d regions of the X-ray photoelectron spectra of PtMo/C electrocatalysts. PtMo/C catalyst A (top) and PtMo/C catalyst C (bottom).

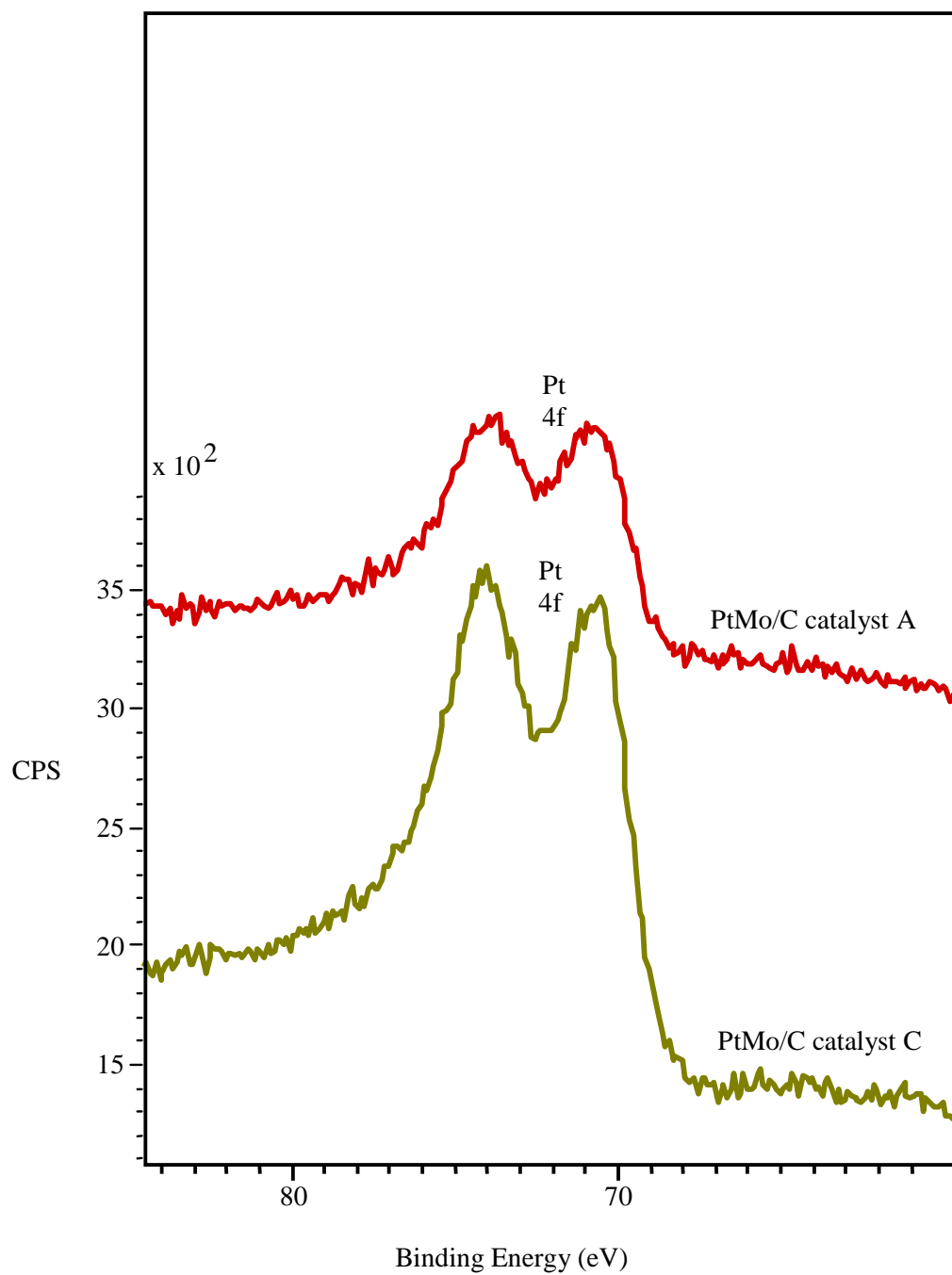


Figure 1b. Pt 4f regions of the X-ray photoelectron spectra of PtMo/C electrocatalysts. PtMo/C catalyst A (top) and PtMo/C catalyst C (bottom)

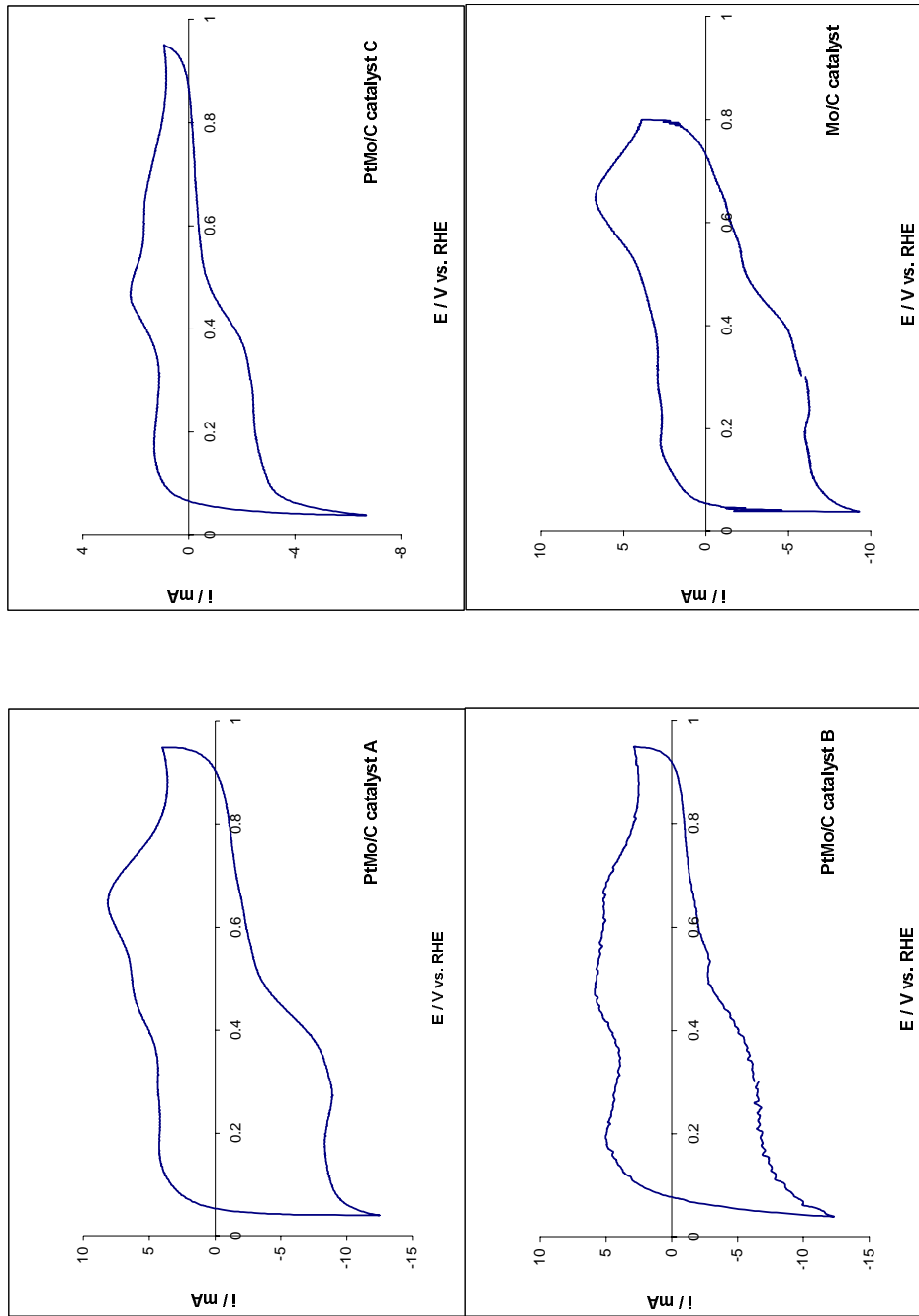


Figure 2. Cyclic voltammograms of the PtMo/C and Mo/C electrodes. 0.1 M H_2SO_4 , room temperature, scan rate 0.1 V/s.

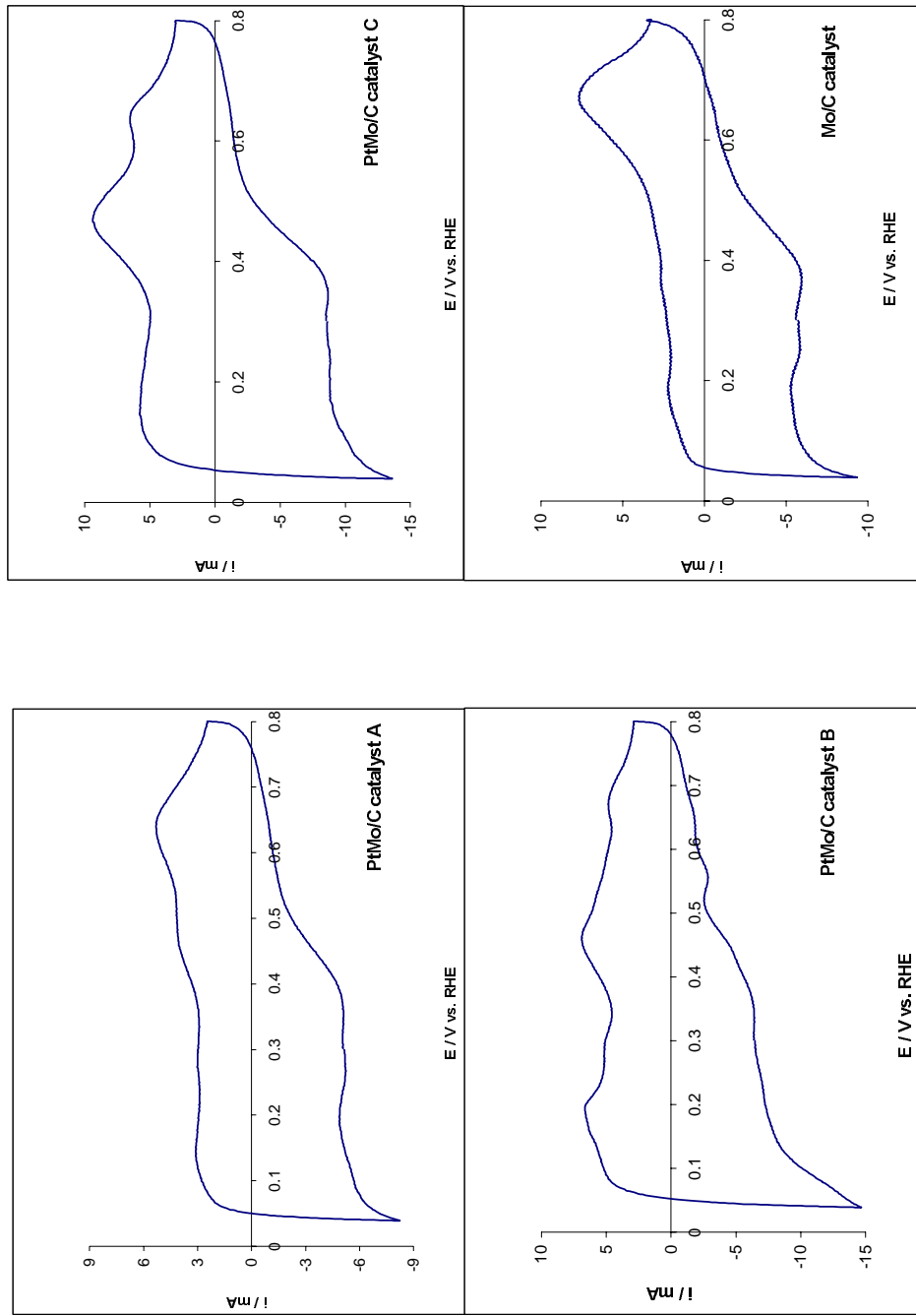


Figure 3. Cyclic voltammograms of the PtMo/C and Mo/C electrodes. 0.5 M H₂SO₄, room temperature, scan rate 0.1 V/s.

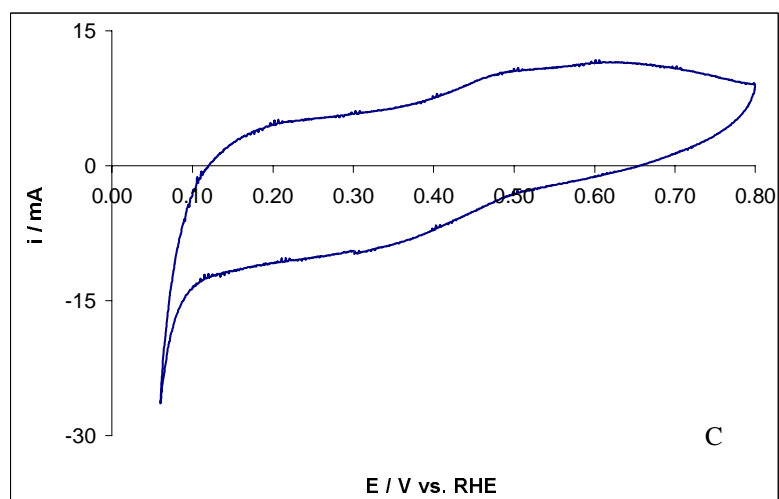
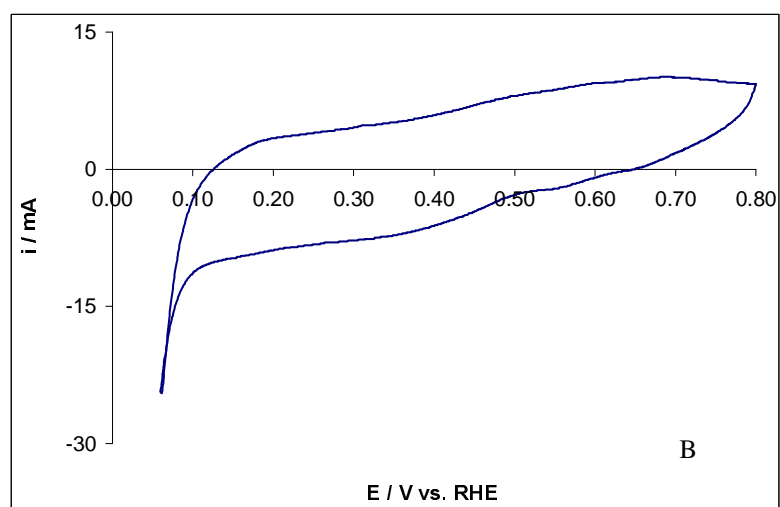
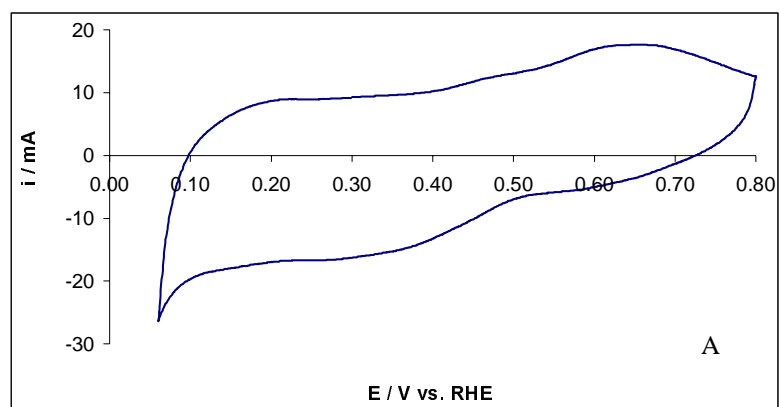


Figure 4. Cyclic voltammograms of the PtMo/C: (a) PtMo/C catalyst A, (b) PtMo/C catalyst B, (c) PtMo/C catalyst C in membrane-electrode assemblies (MEAs). Room temperature, scan rate 0.1 V/s.

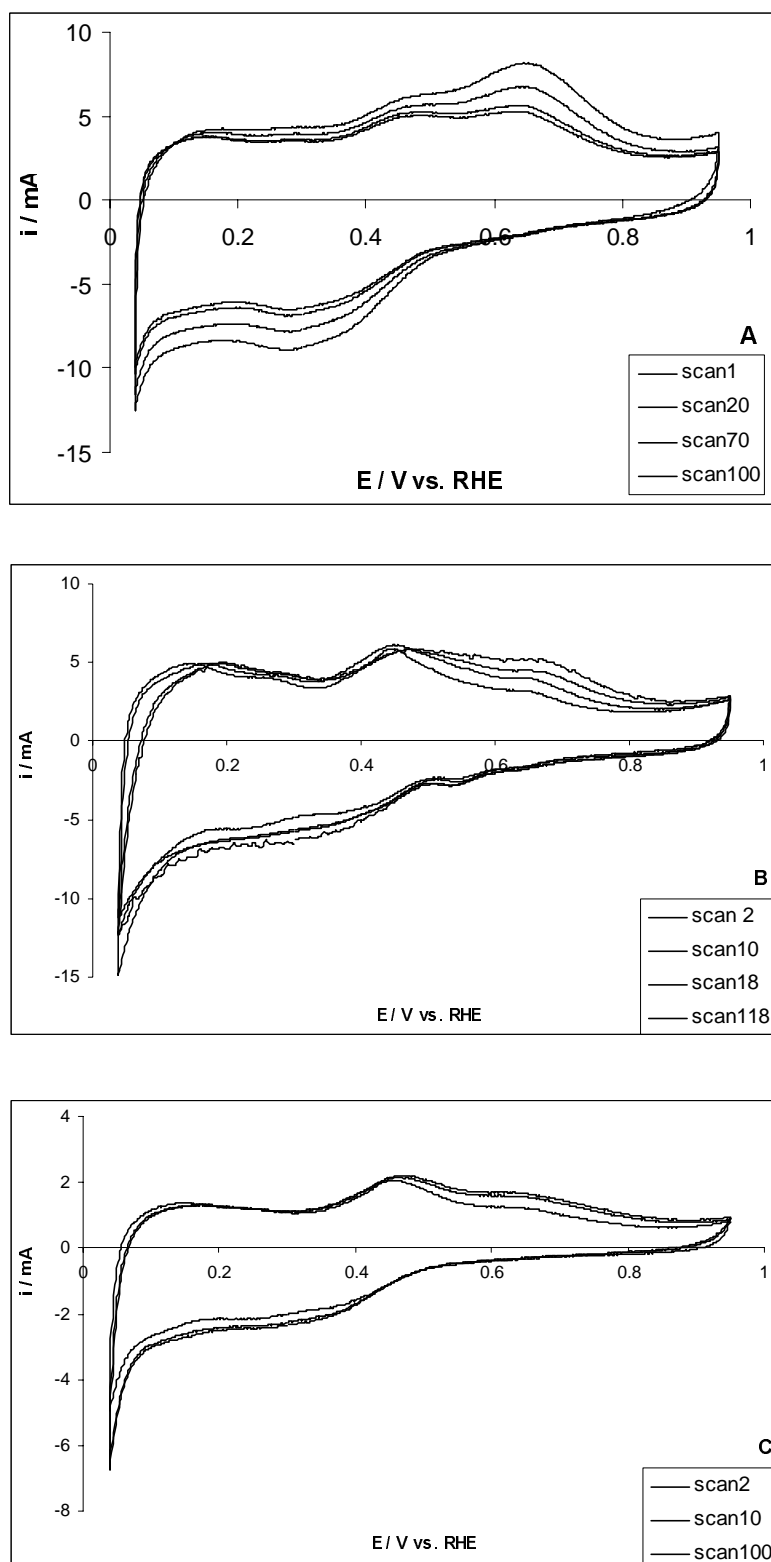


Figure 5. Evolution of the cyclic voltammograms of the PtMo/C electrodes upon cycling in 0.1 M H₂SO₄ at room temperature and scan rate of 0.1 V/s. (a) PtMo/C catalyst A, (b) PtMo/C catalyst B, (c) PtMo/C catalyst C

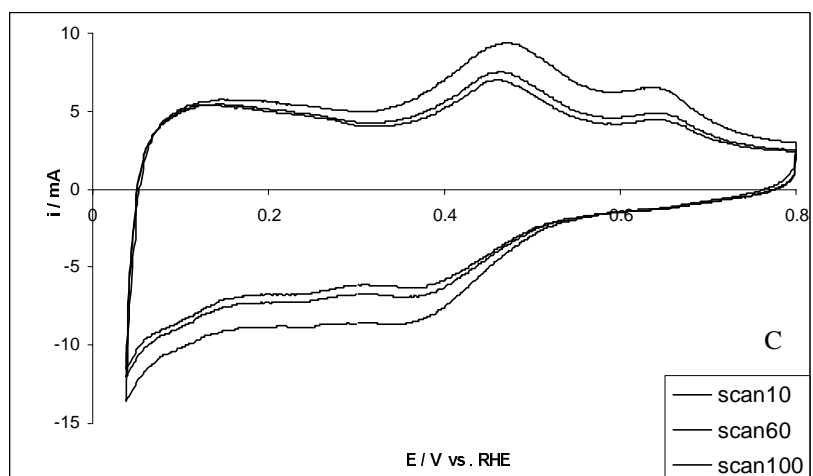
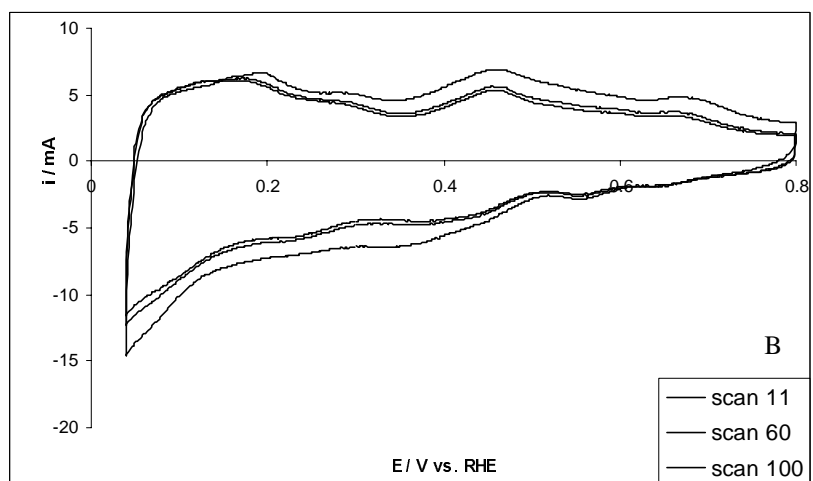
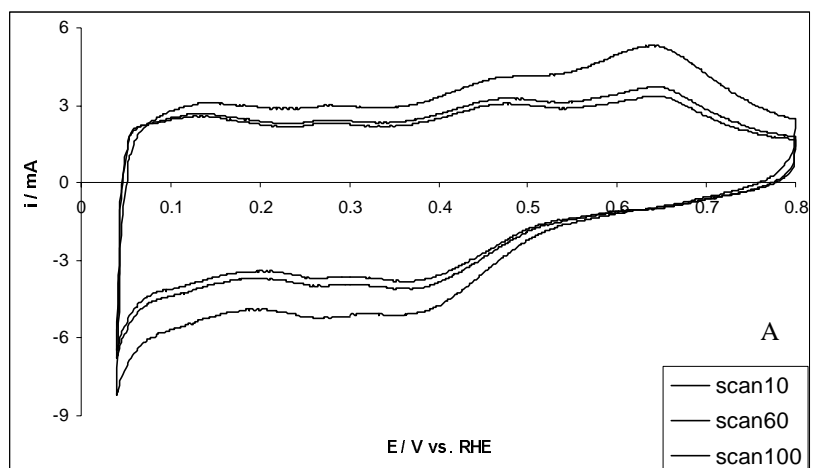


Figure 6. Evolution of the cyclic voltammograms of the PtMo/C electrodes upon cycling in 0.5 M H₂SO₄ at room temperature and scan rate of 0.1 V/s. (a) PtMo/C catalyst A, (b) PtMo/C catalyst B, (c) PtMo/C catalyst C.

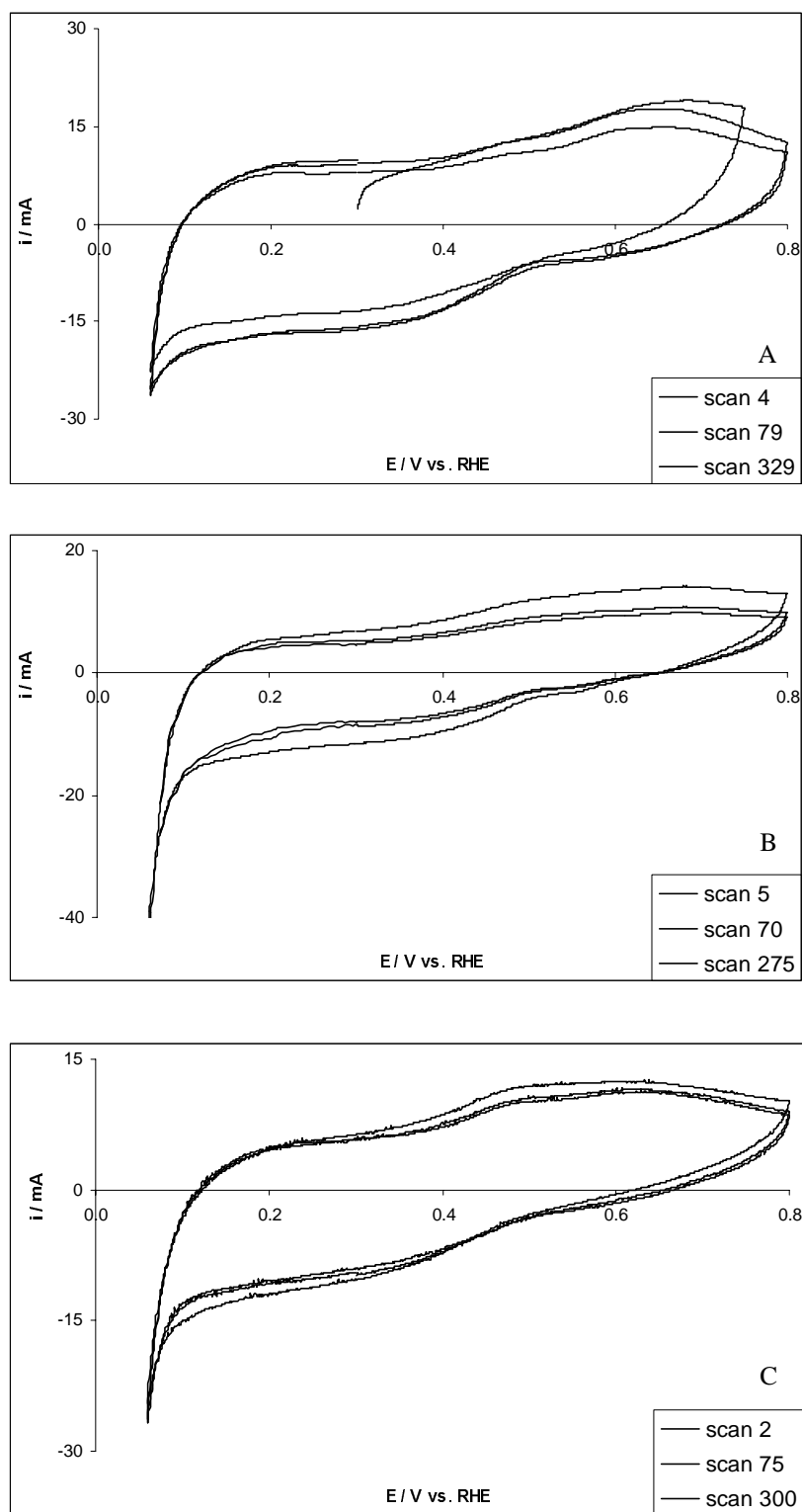


Figure 7. Evolution of the cyclic voltammograms of the PtMo/C electrodes upon cycling in membrane-electrode assemblies (MEAs) at room temperature and scan rate of 0.1 V/s. (a) PtMo/C catalyst A, (b) PtMo/C catalyst B, (c) PtMo/C catalyst C.

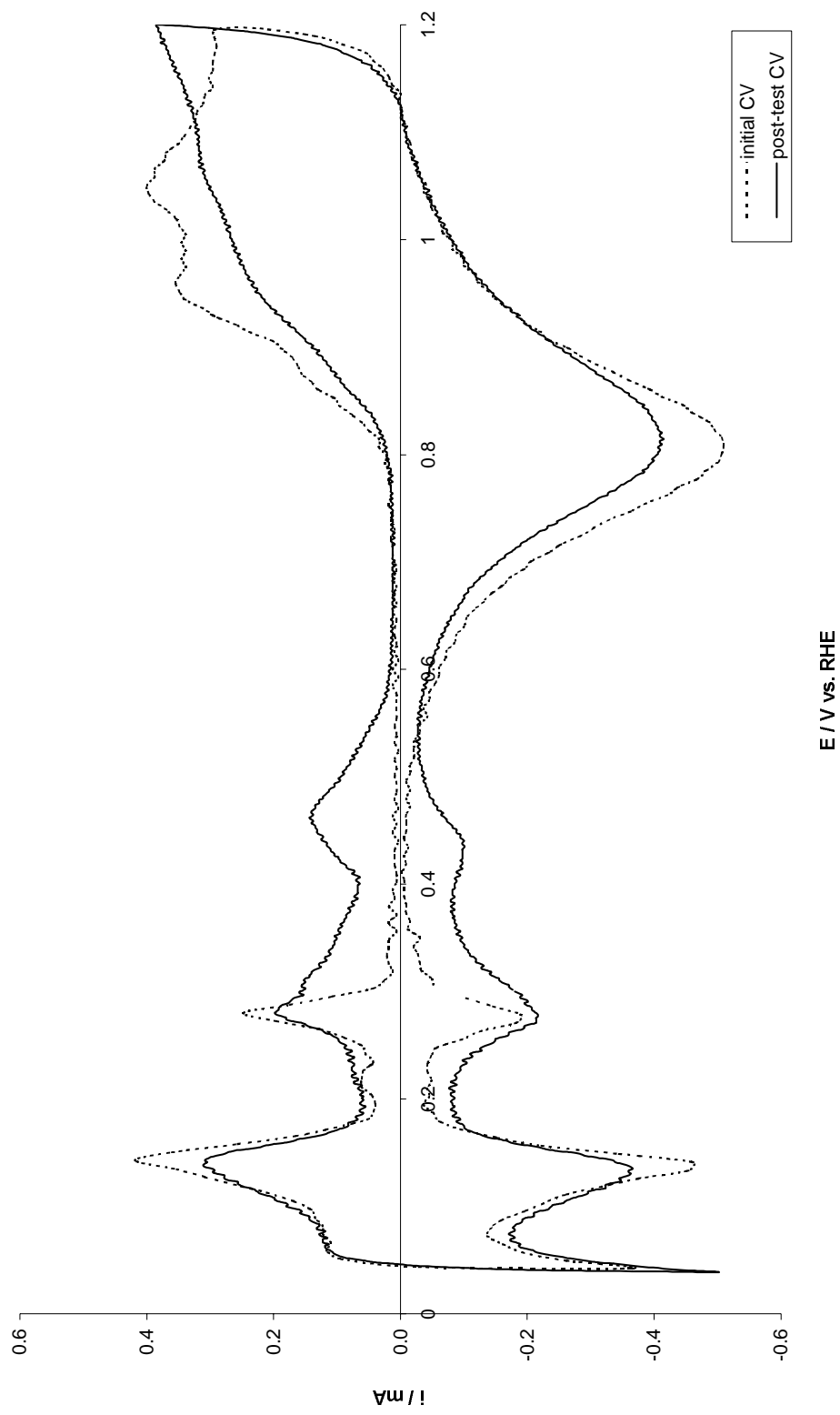


Figure 8. Cyclic voltammograms of a smooth Pt test electrode before (dotted line) and after (solid line) cycling of the PtMo/C catalyst A at room temperature in 0.1 M H_2SO_4 . Scan rate 0.1 V/s.

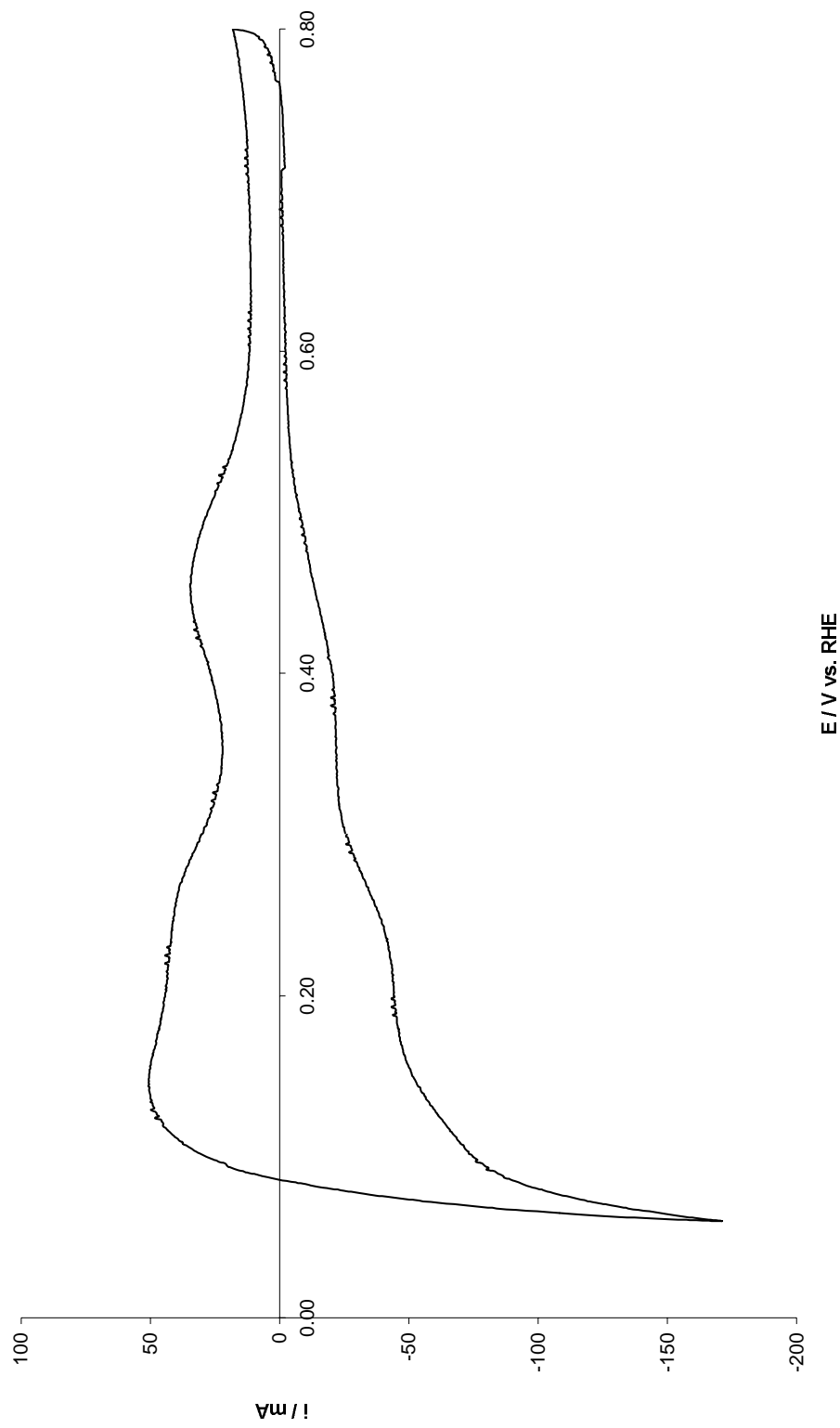


Figure 9. Cyclic voltammogram of the Pt/C cathode after cycling of the PtMo/C catalyst C anode at room temperature in the MEA arrangement. Scan rate 0.1 V/s.

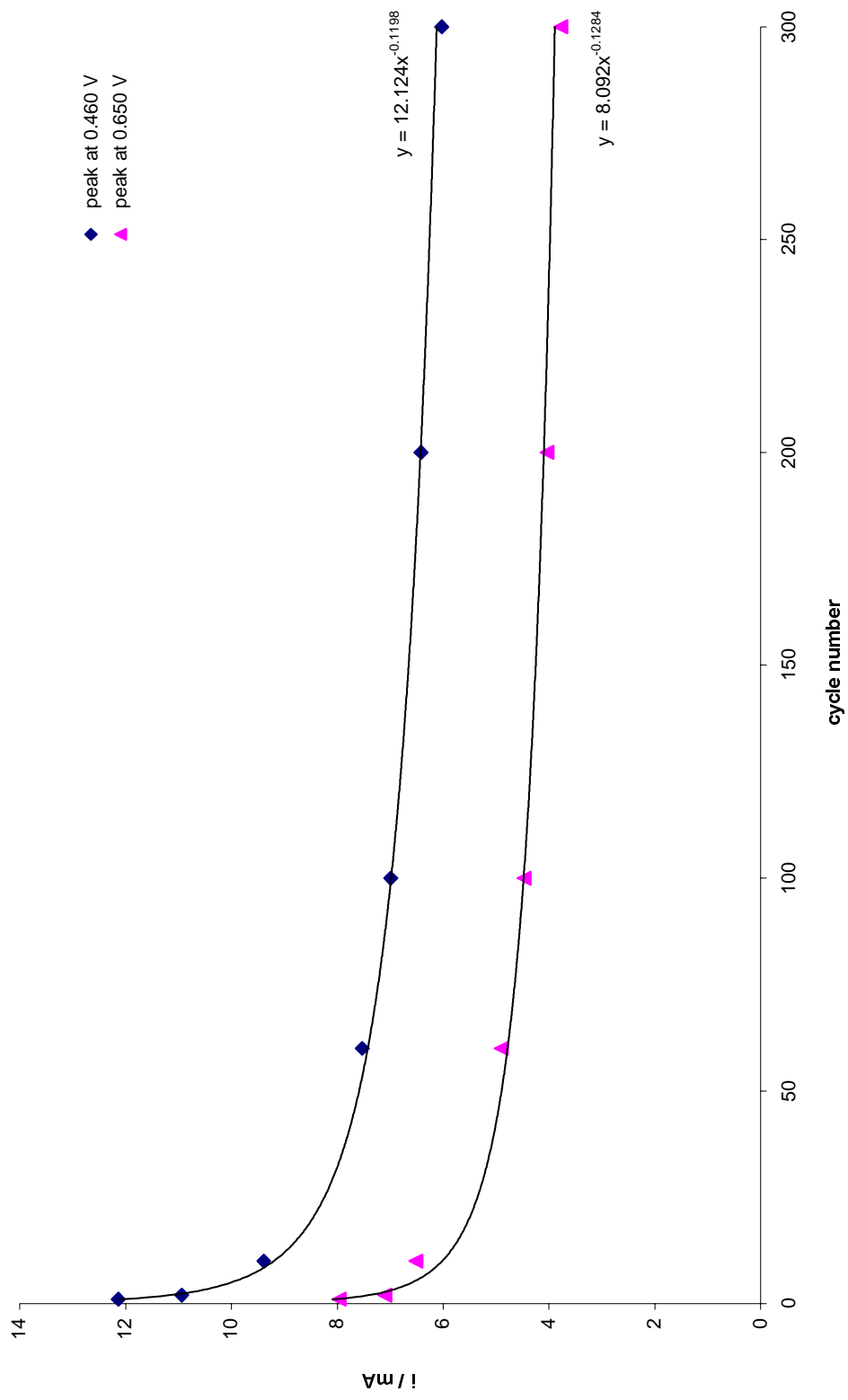


Figure 10. Power function approximation of the dependence of the peak current on cycle number for PtMo/C catalyst C upon cycling in 0.5 M H₂SO₄ at room temperature and scan rate of 0.1 V/s.

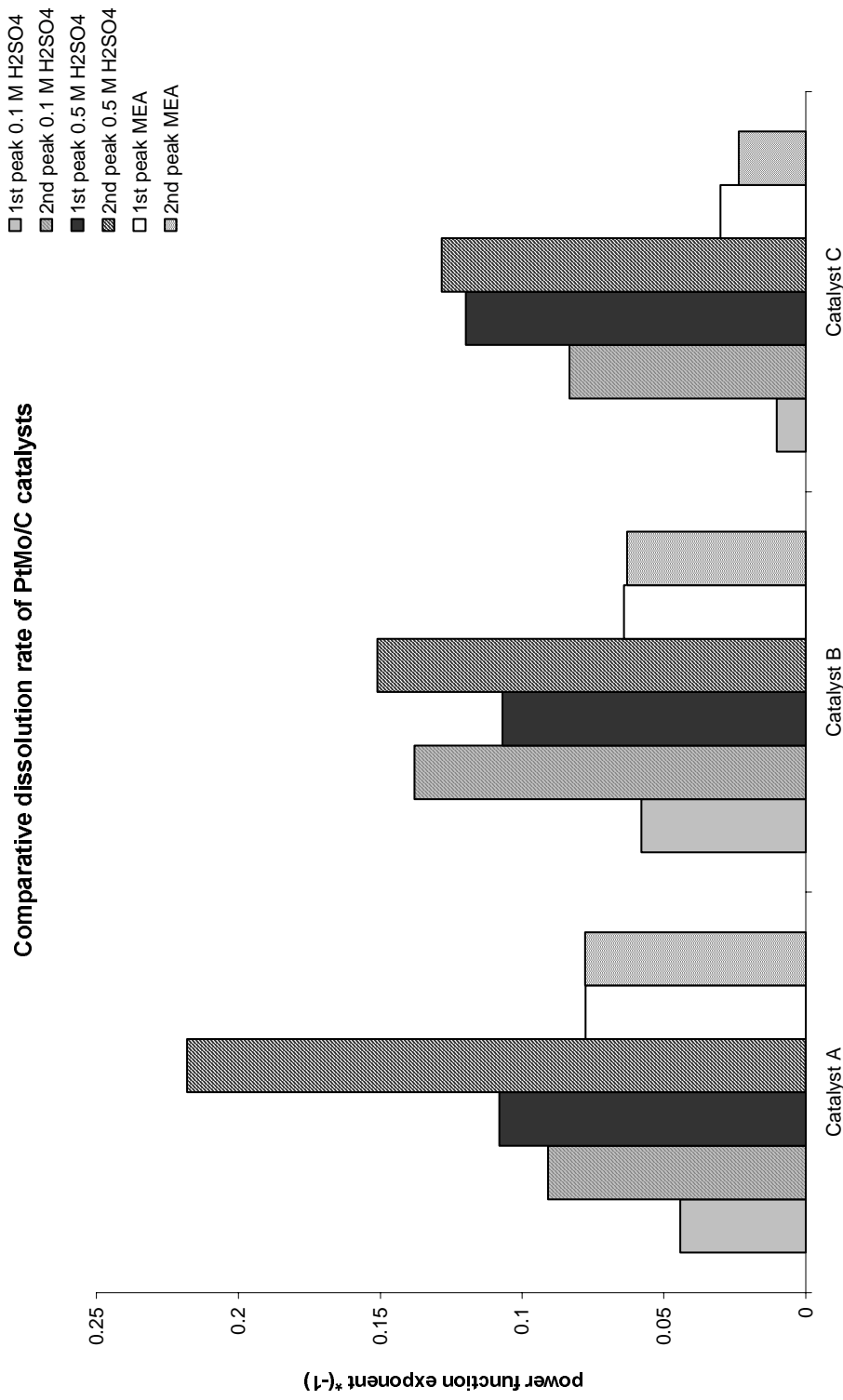


Figure 11. Comparative stability diagram for the synthesized PtMo/C electrodes in 0.1 M and 0.5 M H₂SO₄ as well as in MEAs.

REFERENCES

1. B.N. Grgur, G. Zhuang, N.M. Markovic, P.N. Ross, *J.Phys.Chem. B*, 101 (1997) 3910.
2. B.N. Grgur, N.M. Markovic, P.N. Ross, *J.Phys.Chem. B*, 102 (1998) 2494.
3. M. Götz, H. Wendt, *Electrochim.Acta*, 43 (1998) 3637.
4. B.N. Grgur, N.M. Markovic, P.N. Ross, *Electrochemical Society Proceedings*, 98-27 (1999) 176.
5. B.N.Grgur, N.M. Markovic, P.N. Ross, *J.Electrochem.Soc.*, 146 (1999) 1613.
6. S. Mukerjee, S.J. Lee, E.A. Ticianelli, J. McBreen, B.N. Grgur, N.M. Markovic, P.N. Ross, J.R. Giallombardo, E.S. De Castro, *Electrochem. and Solid State Lett.*, 2 (1999) 12.
7. E.A. Ticianelli, S. Mukerjee, S.J. Lee, J. McBreen, J.R. Giallombardo, E.S. De Castro, *Electrochemical Society Proceedings*, 98-27 (1999) 162.
8. T. Zawodzinski, J. Bauman, T. Rockward, P. Haridoss, F. Uribe, S. Gottesfeld, *Electrochemical Society Proceedings*, 98-27 (1999) 200.
9. S. Mukerjee, R.C. Urian, *Electrochim.Acta*, 47 (2002) 3219.
10. S. Ball, A. Hodgkinson, G. Hoogers, S. Maniguet, D. Thompsett, B. Wong, *Electrochem. and Solid-State Lett.*, 5 (2002) A31.
11. G. Samjeské, H. Wang, T. Löffler, H. Baltruschat, *Electrochim.Acta*, 47 (2002) 3681.
12. E.M. Crabb, M.K. Ravikumar, Y. Qian, A.E. Russell, S. Maniguet, J. Yao, D. Thompsett, M. Hurford, S.C. Ball, *Electrochem. and Solid-State Lett.*, 5 (2002) A5.
13. D.C. Papageorgopoulos, M. Keijzer, F.A. de Bruijn, *Electrochim.Acta*, 48 (2002) 197.
14. R.C. Urian, A.F. Gullá, S. Mukerjee, *J.Electroanal.Chem.*, 554-555 (2003) 307.
15. E.I. Santiago, G.A. Camara, E.A. Ticianelli, *Electrochim. Acta*, 48 (2003) 3527.
16. Z. Hou, B. Yi, H. Yu, Z. Lin, H. Zhang, *J. Power Sources*, 123 (2003) 116.
17. S. Mukerjee, R.C. Urian, S.J. Lee, E.A. Ticianelli, J. McBreen, *J. Electrochem.Soc.*, 151 (2004) A1094.
18. E. I Santiago, M.S. Batista, E.M. Assaf, E.A. Ticianelli, *J.Electrochem.Soc.*, 151 (2004) A944.
19. J.A. Shropshire, *J.Electrochem.Soc.*, 112 (1965) 465.
20. Z. Jusys, T.J. Schmidt, L. Dubau, K. Lasch, L. Jörissen, J. Garche, R.J. Behm, *J. Power Sources*, 105 (2002) 297.
21. S.J. Cooper, G. Hoogers, patent WO 00/35037, 1998.
22. T.J. Schmidt, M. Noeske, H.A. Gasteiger, R.J. Behm, P. Britz, W. Brijoux, H. Bönnemann, *Langmuir*, 13 (1997) 2591.
23. C. Roth, M. Goetz, H. Fuess, *J. Appl. Electrochem.*, 31 (2001) 793.
24. J.W. Long, R.M. Stroud, K.E. Swider-Lyons, D.R. Rolison, *J.Phys.Chem.B*, 104 (2000) 9772.
25. E. Auer, A. Freund, T. Lehmann, K.-A. Starz, R. Schwarz, U. Stenke, US patent 6.007.934, 1999.
26. D.C. Papageorgopoulos, M.P. de Heer, M. Keijzer, J.A.Z. Pieterse, F.A. de Bruijn, *J.Electrochem.Soc.*, 151 (2004) A763.
27. J. Perez, A.L.N. Pinheiro, E.R. Gonzales, E.A. Ticianelli, patent BR 9702816-9, 1997.
28. X-ray photoelectron spectra were interpreted using NIST database: <http://srdata.nist.gov/xps/> and J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, *Handbook of X-ray photoelectron spectroscopy*, Ed. J. Chastain, Perkin Elmer Corporation, Physical Electronics Division, Eden Prairie, Minnesota, 1992.
29. (a) F.A. de Bruijn, G.B. Marin, J.W. Niemantsverdriet, W.H.M. Visscher, J.A.R. van Veen, *Surface and Interface Anal.*, 19 (1992) 537; (b) J.W. Niemantsverdriet, *Spectroscopy in catalysis. An introduction*, VCH, Weinheim, 1995, Chapter 3.
30. A.F. Holleman, E. Wiberg, *Inorganic Chemistry*, Academic Press, 2001, p. 1382-1402.

31. K. Kinoshita, *Carbon. Electrochemical and physicochemical properties*, John Wiley&Sons, 1988, Chapters 6 and 7.