

## Synthesis and Characterization of Electrolyst Powders for Application in PEM Fuel Cells

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**Abstract.** The *Bönnemann* method was chosen to synthesize carbon-supported Pt-Ru-Mo electrocatalyst powders, as this method leads to highly-dispersed nanoparticles with an average particle size of approximately 2 nm. Structural characterization of the resulting catalysts was done by the following techniques: X-rays fluorescence analysis (XFA) and nanosize-energy dispersive X-rays analysis (nano-EDX) to obtain information about noble metal loading and composition as well as X-rays diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) to determine structure, dispersion and crystallite size of the nanoparticles. X-rays photoelectron spectroscopy (XPS) was applied to detect amorphous phases and to determine the oxidation states of Pt, Ru and Mo. The morphology of membrane electrode assemblies, prepared by a spraying technique, was checked by scanning electron microscopy (SEM). For the determination of the electrocatalytic activity E/i curves in single cell arrangements were recorded using both H<sub>2</sub>/CO mixtures and methanol as feed gases.

### Introduction

Global climate changes and the necessity of environmental protection will lead to a technological revolution in this new century. Among those new technologies one of the most promising for effective electricity production and, at least, partly substitution of the internal combustion engine (ICE) is the fuel cells technology [1].

Fuel cells are electrochemical devices that transform chemical energy directly into electricity and heat, in an environmental friendly way producing 10 times less or no emissions than an ICE. In this context, low-temperature proton exchange membrane fuel cells (PEMFC) have been quoted as the most promising technology to substitute the ICE and to create decentralized power plants for stationary power generation. A great challenge for this technology is the development of new electrocatalysts presenting lower contamination by adsorbed CO, while operating with reformat gas or methanol (DMFC: direct methanol fuel cell) [2-4].

The synthesis of new binary and ternary electrocatalyst systems, e.g. Pt-Mo [5], Pt-Sn [6] and Pt-Ru-W [7], by various methods has been reported by different authors. These catalyst

systems show less sensitivity to CO poisoning compared with pure platinum. One well-known method to synthesize highly-dispersed nanoparticles with a very small particle size distribution is a colloid method originally developed by Bönemann et al. [8,9]. The suitability of this method for the preparation of supported nanoscale systems was shown by Schmidt and coworkers [10]. Besides electrochemical investigations spectroscopic, microscopic and diffraction methods were applied to learn more about the real structure of the catalysts in question [11, 12, 13].

In the work presented here, a ternary Pt-Ru-Mo catalyst was prepared by a slightly-modified *Bönemann* method according to reference [14, 15]. The *Bönemann* method was chosen, as crystallite sizes between 1.5 and 2.5 nm can be achieved showing high electrocatalytic activities due to their favorable surface-to-bulk ratio. Both structural and electrochemical characterization of the resulting catalysts was done to get some idea of the effect of the catalysts nanomorphology on the electrocatalytic activity. For structural characterization, among others, X-rays diffraction and high resolution transmission electron microscopy were applied to investigate the crystallite sizes, particle size distribution and the particle dispersion on the support. Scanning electron microscopy was used to obtain more information on the morphology of the membrane electrode assemblies (MEA), while the electrochemical characterization of the catalysts in question was done by polarization ( $E/i$ ) curves.

## Experimental

### *Synthesis of the electrocatalyst by the Bönemann method:*

First  $\text{NR}_4\text{X}$ -stabilized colloidal Pt-X precursors were prepared via the reduction of  $\text{PtCl}_2$ ,  $\text{RuCl}_3$  and  $\text{MoCl}_5$ . Then a suspension of Vulcan XC-72 (Cabot inc.) in millipore water was impregnated with an appropriate amount of the colloidal solution. Details of the synthesis can be found in [15].

### *Characterization of the electrocatalyst powder by XFA, XRD, TEM and XPS:*

Metal loading and composition of the supported catalysts were measured using an Xlab 2000 (Spectro analytical instruments GmbH).

X-rays powder diffraction was carried out on a STOE STADI-P powder diffractometer, with germanium monochromatized  $\text{CuK}_\alpha$  radiation and a position-sensitive detector with  $40^\circ$  aperture in transmission mode.

A Philips CM 20 with an acceleration voltage of 200 kV and tungsten cathode was applied for high resolution images of the supported catalysts. Additionally the microscope was equipped with a nano-EDX device to check the catalysts composition in nm-sized regions. Samples were prepared by suspending the catalyst powder in methanol and depositing a drop of the suspension on a standard copper grid covered with carbon.

The XPS measurements were carried out on a PHI 5700 MultiTechnique ESCA (Perkin Elmer) with  $\text{AlK}_\alpha$  radiation at a power of 300 W. A suitable pass energy of 11.75 eV was chosen, while a pressure of  $3 \times 10^{-8}$  mbar was maintained within the spectrometer chamber. Samples were prepared by pressing a small amount of the supported catalyst powder into In-foils. The spectra were fitted and evaluated by the standard software Igor Pro (Wavemetrics Inc., Oregon, 1988) using a mixed Gauss-Lorentzian function.

### *Electrochemical investigation in single cells*

The preparation of membrane electrode assemblies (MEA) was carried out using the hot spray method developed by Wilson and Gottesfeld [16] and modified by Götz et al.[14]. According to this method an appropriate amount of ink was prepared for each electrode and sprayed on an area of 25 cm<sup>2</sup> to yield a metal loading of 0.4 mg/cm<sup>2</sup>. The MEA was fit into a commercially available graphite cell block using teflonized carbon paper (Toray TGPR-090) as gas distributor on each electrode. For hydrogen operation, the anode gas was humidified at a temperature of 85°C using a hydrogen flow of 150mL/min. Feed gas at the cathode was dry oxygen (75 mL/min) at a cell temperature of 75°C.

For methanol operation, 1 mL/min of a 1 M aqueous methanol solution was evaporated and fed into the cell by a support gas flow of 35 mL/min of nitrogen. The cell temperature of 95°C was maintained, and cathode feed gas was dry oxygen. The minimum operation time for one MEA in a single cell test was 10 days. The catalytic activity of the system was measured by recording the polarization (E/i) curves.

## **Results**

A detailed characterization of the Pt-Ru-Mo electrocatalyst should cover at least three different fields of investigation, including chemical analysis (bulk composition of the catalyst was checked by XFA and nano-EDX), structural and electrochemical characterization.

### *X-rays fluorescence analysis (XFA)*

The noble metal loading and stoichiometry were verified by XFA measurements. The total noble metal loading was 7.8 wt% and the molar ratio of Pt and Ru was 1:1. The results (Table 1) are suitable according to the stoichiometric amounts employed for the synthesis.

Table 1: Metal loading and molar composition of noble metals by XFA.

Element	Wt%	At. %
Pt	5.0	48
Ru	2.8	52
Noble metal loading	7.8 (total)	

### *Nanosize-energy dispersive X-rays analysis*

The transmission electron microscope is equipped with a nano-EDX device to perform analyses in small areas of the specimen in order to verify the stoichiometry of the nanocrystals. The composition of the nanocrystals was almost the same for both catalysts according to a Pt-Ru-Mo 1:1:1 stoichiometry (Table 2).

Table 2: Nano-EDX analysis of the catalysts.

Element	PtRuMo (sample 1)		PtRuMo (sample 2)	
	Wt%	At%	Wt%	At%
Pt	52	35	49	32
Ru	21	28	25	33
Mo	27	37	26	35

### Scanning electron microscopy (SEM)

The powder morphology revealed by SEM (Figure 1 and 2) presents agglomerates with a medium size of 50  $\mu\text{m}$  in both samples. Due to the resolution limit in conventional SEM, it was not possible to identify the nanoparticles on the carbon support. Figure 3 shows the triple reactional interface of a MEA. By the spraying process a micropore structure is produced facilitating the diffusion of educts and products during the reaction. Anode and cathode side of the MEA exhibit the same structure, as can be seen in Figure 4.

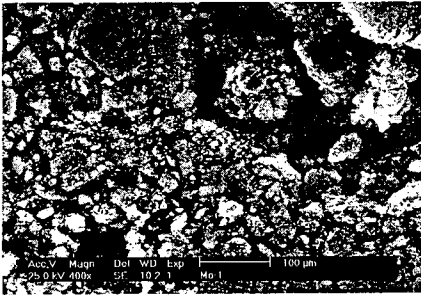


Figure 1 : SEM micrograph of the Pt-Ru-Mo catalyst (sample 1)

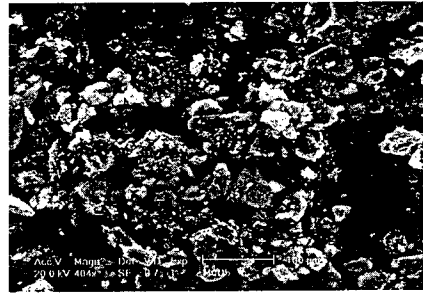


Figure 2 : SEM micrograph of the Pt-Ru-Mo catalyst (sample 2)

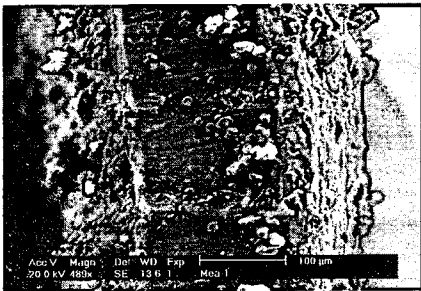


Figure 3: MEA with anode and cathode thickness of ca. 20  $\mu\text{m}$ .

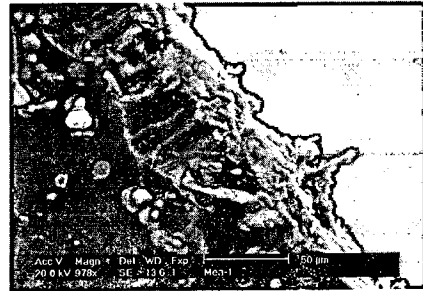


Figure 4: Anode structure of the MEA similar to the cathode structure.

### High resolution transmission electron microscopy (HRTEM)

Nanocrystallites with an average diameter of approximately 2 nm are displayed in Figure 5. The catalytic active particles are highly-dispersed on the support grains for both samples. In comparison with the results for PtRu published by Schmidt et al.[10] slightly bigger particle sizes were found, perhaps due to the addition of Mo.

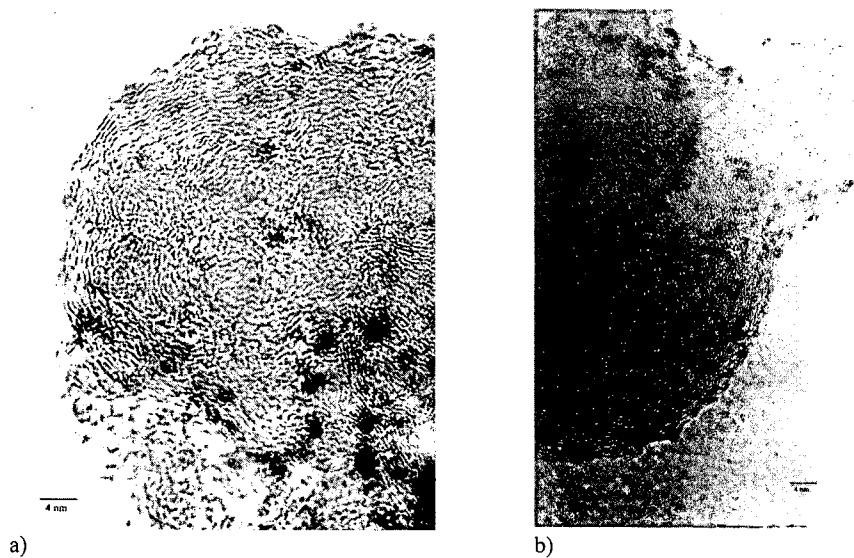


Figure 5: HRTEM images of the Pt-Ru-Mo catalysts:  
 a) PtRuMo (sample 1) crystallite size =  $2.0 \pm 0.5$  nm.  
 b) PtRuMo (sample 2) crystallite size =  $2.0 \pm 0.5$  nm

#### *X-rays diffraction (XRD)*

The diffractograms of the ternary catalysts reveal platinum as the only crystalline phase showing reflections according to the ICDD data base. No evidence of other metallic phases or crystalline oxide species was found. Almost complete reduction of the educts was achieved, as no reflections of any metal chlorides appear in the patterns.

#### *X-rays photoelectron spectroscopy (XPS)*

The surface composition of the catalysts was investigated by X-rays photoelectron spectroscopy. As the particles are very small, the approximation of obtaining nearly bulk information can be made. The results of the measurements are presented in Table 3. For the 4f signal of platinum two binding energies (BE) can be obtained corresponding to metallic platinum and a Pt oxide species. Deconvolution of the Ru 3p peak gave two distinguishable peak pairs with BEs of 463.1 and 465.6 eV according to an oxide and a hydrous oxide species. For molybdenum only oxidized species can be found that are not easy to ascribe to a specific compound. The platinum signal shows a shift to higher binding energies which can be either explained by the small particle size or an alloy formation.

Table 3: XPS measurements of PtRuMo (sample 1)

Element	Binding energy (eV)	State
Platinum	72.1	Pt
Pt 4f	74.2	PtO <sub>2</sub>
Ruthenium	463.1	RuO <sub>2</sub>
Ru 3p	465.6	RuO <sub>2</sub> × H <sub>2</sub> O
Molybdenum	232.1	(NH) <sub>4</sub> MoO <sub>4</sub>
	232.8	MoO <sub>3</sub>

### Polarization curves ( $E/i$ )

The MEAs were operated in a fuel cell system with 25 cm<sup>2</sup> active electrode area first with pure hydrogen for at least ten days, then with H<sub>2</sub>/CO mixtures to simulate reformat gas and afterwards with methanol. Sample 1 shows a decrease of the CO-sensitivity compared with pure Pt catalysts. However, the performance with H<sub>2</sub>/CO mixtures and methanol is still worse than the commercial Pt-Ru catalyst (E-TEK inc.), probably due to the not yet optimized preparation (Fig. 6 and 7). In accordance with Lasch et al [17] it was found that ternary catalysts are able to sustain higher current densities than the binary ones, as can be seen in Fig. 6 and 7.

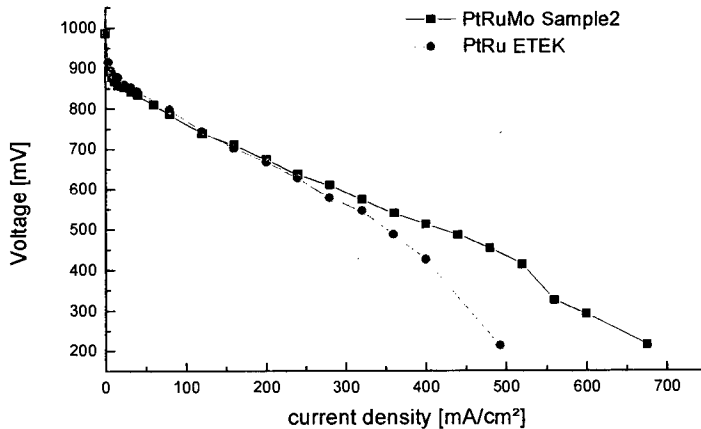


Fig. 6: Polarization curves for PtRuMo (sample 2) and PtRu (1:1) ETEK with pure hydrogen.

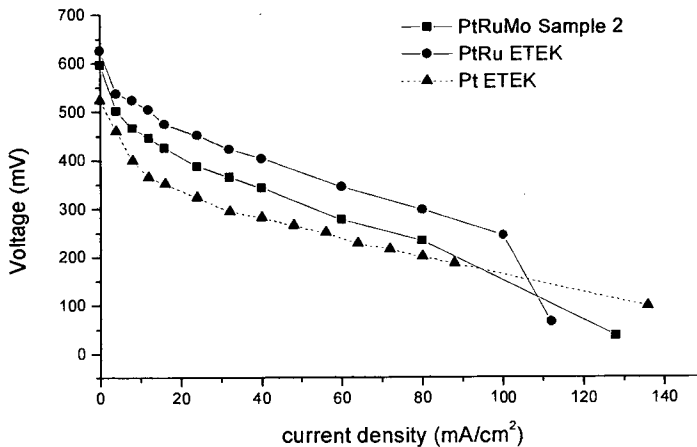


Fig. 7: Polarization curves for PtRuMo (sample 2), PtRu (1:1) ETEK and Pt ETEK with pure methanol 1 mol.L<sup>-1</sup>.

## Conclusion

The *Bönnemann* method is an effective synthesis for the preparation of new catalyst systems for PEMFC and DMFC. Highly-dispersed nanocrystals with an average size of 2 nm were obtained and characterized in detail by spectroscopy, microscopy and diffraction in the present work. The electrocatalytic activity of the synthesized Pt-Ru-Mo catalysts for reformate and methanol oxidation was evidenced by E/i curves showing a very promising system to be optimized.

Scanning electron microscopy (SEM), nanosize-energy dispersive analysis (nano-EDX), X-rays fluorescence analysis (XFA), X-rays diffraction (XRD), X-rays photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM) were used for the structural characterization of the ternary catalyst systems. Electrochemical data were obtained by recording E/i curves in single cell arrangements. Only both, structural and electrochemical characterization together, will result in a detailed understanding of the effect of the structure on the electrocatalytic activity of catalysts in real fuel cell systems.

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