SYNTHESIS AND CHARACTERIZATION OF Pt/POLYOXOMETALATES COMPOSITE CATALYSTS FOR PEM FUEL CELLS

FABIO CIUFFREDA

Instituto Superior Técnico, Universidade Técnica de Lisboa

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ABSTRACT

This thesis work was focused on synthesis and characterization of catalytic supports of PEM-Fuel Cells, based on polioxometalates (POM), starting from heteropolyacids. Two kinds of ink preparation were carried out for the catalytic supports: mixing and impregnation; electrochemical and physical characterization of the synthesized compounds was then performed. First of all, a physical characterization has been done (SEM-XRD, TEM, XRD, Uv-VIS, IR) to discover the sample morphology and also to try to know which one should work better, after that it was continued with electrochemical analysis. Three types of electrochemical analysis were made for each sample: cyclic voltammetry (CV) to see which and how many reactions are involved on to analysed sample and which potentials; linear sweep voltammetry (LSV) with rotating disk electrode (RDE) to discover the amount of current that sample is capable to provide, and finally the CO-stripping useful to analyse the dynamics of CO poisoning catalyst. Different samples were prepared with different amounts of Cs and different Pt/POM mass ratios to see which combination can provide the better electrochemical performance combined with a good durability. Was also performed an electrochemical impedance spectroscopy and polarization curve directly in Fuel cell. These latter tests have confirmed the improved performance of electrodes modified with POMs studied in this thesis, leaving an open door for future development in this research field.

Keywords: Proton Exchange Membrane Fuel Cell, Pt/Polyoxometalates, fuel cell catalytic support, Heteropolyacids, hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR), Vulcan XC-72R, Nafion, Ring Rotating Disk Electrode (RRDE), Linear sweep voltammetry, Cyclic voltammetry, Polarization curve, Tafel, Koutecky-Levich.

Introduction:

Polyoxometalates (POMs), which are defined as early transition metal clusters, are considered as one of the most growing fields of research and development in electrocatalysis thanks to its particular structure (Keggin type) able to provide a good catalyst dispersion when used as catalyst support. Polyoxometalates (POMs) are made of oxygen and early transition metals (e.g., M = V, Nb, Ta, Mo, W) at their highest oxidation states. They may also contain a variety of heteroatoms (e.g., X = P, As, Si, Ge). POMs are molecular oxides which are distinguishable from the majority of metal oxides\(^1\). They may contain tens to hundreds of metal atoms that reach nuclearities as high as 368 metal atoms in one single cluster molecule (forming nanoparticles). Berzelius reported the first synthesized POM in the early 19th century. In 1864, Marignac\(^1\) successfully synthesized
silicotungstic acid. There are numerous applications of POMs as acid and oxidation catalysts both in homogeneous and in heterogeneous conditions. Polyoxometalates (POMs) can be classified as isopolyanions (IPAs) and heteropolyanions (HPAs). POMs are frequently formed in aqueous media. However, in some cases, the assembly of the oxoanions may also occur in non-aqueous media or even in the solid state such as in minerals\textsuperscript{iii}. The stability of POMs in aqueous or non-aqueous solvents is generally measured by their ability to retain their structural identities and avoid degradation or transformation to other forms. Nevertheless, POMs under particular conditions may undergo degradation, and thanks to modern techniques, we now have a better understanding of the mechanisms under which POMs transform from one state to another during the degradation process. The two basic structures of POMs are Keggin (X/M = 1/12) and Dawson (X/M = 2/18) structures. The assembly of two or several Keggin or Dawson fragments leads to formation of other complex structures. The structure\textsuperscript{iv} of these compounds contains a high atomic proportion of oxygen atoms that are linked to a different cluster, sometimes hydrogen and atoms of at least two other elements. One of these is a transition metal atom from V or VI group in its high oxidation states, e.g. V\textsuperscript{5+}, Mo\textsuperscript{6+}, W\textsuperscript{6+} called “addenda atom”. The second is called “heteroatom” and its proportion is much smaller, e.g. P\textsuperscript{5+} and Si\textsuperscript{4+}. The existence of the enormous variety of polyoxometalates is due to the fact that more than half of the elements of the periodic table can be incorporated within the structure of these compounds, such as \([P_2Mo18O62]^{6-}\), \([SiMo2W10O40]^{4-}\), \([PMo11VO40]^{4-}\) etc. On the contrary, only the elements that support oxygen coordination from 4 to 6 and whose with atomic radius small enough to fit within a structure of octahedral symmetry can be used as heteroatoms. These structures contain anions packed around the cations in geometries governed by the relationship between the radii. POMs can be divided into two large families: the isopolyoxometallates (or isopolyanions), and heteropolyoxometallates or (heteropolyanions):

- **Isopolyanions**: \([M_mO_y]^{p-}\)
- **Heteropolyanions**: \([X_xM_mO_y]^{q-}\) (where \(x \leq m\))

The composition of the cluster can be very complex because various elements M can be present in the structure. A general classification of the different structures is given below. This classification is mainly focused on polyoxometalates with Keggin-type structure that have found important applications in catalysis and are the subject of this thesis.

The crystal structure of a heteropolycompound is governed by two basic principles\textsuperscript{v}:

- Any atom M is located in the center of polyhedral cavities, usually octahedral, forming polyhedra of the type MO\textsubscript{x} and their coordination through pπ-dπ bonds. The oxygen atoms are located at the top.
- The polyoxometalates are characterized by octahedral MO\textsubscript{6} units that can have no more than two vertices free by oxygen atoms.
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Figure 1: Basic unit $MO_6$ and the three possible unions between two octahedral units, where each corner represents oxygen position A) corner sharing, B) edge sharing and C) face sharing.

The structure of heteropolyanions is characterized by the rearrangement of polyhedra $MOX$ (where $M = V, Mo, W, Nb$ or more rarely $Ta$), or more polyhedra around a central $XO_n$ (where $X = P, Si, Ge$ in rare cases, $As, Co$) which may have symmetry $Td, O,$ or $Ih$. As shown in Figure 2, it is possible to distinguish different classes according to the different symmetry of the central heteroatom $X$ in the polyhedron:

Figure 2: From left: Wells – Dawson $[X_2M_{18}O_{62}]^{2n-16}$ (Td); Anderson - Evans $[XM_6O_{24}]^n$ (Oh); Dexter - Silverton $[XM_{12}O_{42}]^{n-12}$ (Ih); Keggin $[XM_{12}O_{40}]^{n-8}$ (Td).

Another important feature of polyoxometalates is the formation of salts, which can be obtained by titration of the acid with a metallic salt, for example with a chloride or a carbonate. Cations as $Cs^+$, $NH_4^+$, or $Rb^+$ occupy the sites of $H_3O^+$ in the secondary structure of the polyoxometalates. The salts that can be synthesized are classified into two groups according to the size of countercation: group A is associated with cations of small size such as $Na^+$ and $Cu^+$, and group B includes cations as large as $Cs^+$ or $NH_4^+$. In general, salts and hydrogenated forms of group A have a low surface area, which reflects their solubility in water, while group B salts are insoluble in water, have a high surface area and strong acidity. The properties of aggregates of the B group are particularly interesting because they can disperse, within the micro-mesoporous structure (tertiary structure), particles of Pt as catalysts. Okuhara et al. have proposed the model for the microstructure of the Cs$^+$ salts reported in Figure 3. The primary structure is always a Keggin structure. The arrangement of the primary structure together with Cs$^+$ forms the secondary structure, which corresponds to the microcrystallites. During the preparation step, the microcrystallites form aggregates with dimensions near 1μm. These aggregates are called tertiary structure and possess micropore in the range from micropore to mesopore as
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revealed by N\textsubscript{2} adsorption. The dimension of mesopores varies from 20 to 500 Å, with an area approximately equivalent to 30\% of total area. The rest of measured area is covered by micropore (width < 2nm). In any case, the Cs content precisely controls the pore size of acidic Cs salts\cite{vii}.

![Figure 3: Model for microstructures of Cs salts.](image)

The surface area depends on the countercation, but it is also variable depending on the precipitation and drying process and it changes with the number of substituted protons. The surface area of Cs\textsubscript{x}H\textsubscript{(3+n)}PMo\textsubscript{12-}\textsubscript{n}V\textsubscript{n}O\textsubscript{40} shows a maximum when Cs ratio is between the range of 2.5 and 3.5\textsuperscript{th}. An innovative application of these salts is their use as matrix for obtaining dispersion of Pt nanoparticles, embedded into the pores of the solid acid, in order to realize catalyst layers containing Pt\textsuperscript{x}. These materials show electrocatalytic properties towards a wide range of reaction.

**Experimental section:**

**Reagents:**

- Vulcan XC-72R (E-Tek Division);
- Cesium carbonate, Cs\textsubscript{2}CO\textsubscript{3} (Sigma-Aldrich \geq 99.00\%);
- 20\% HP Pt on Vulcan XC-72R (E-Tek Division);
- Phosphovanadomolibdic acid PVM-1-11; PVM-2-10; (Nippon Inorganic Colour & Chemical CO., LTD.);
- Chloroplatinic acid hexahydrate, H\textsubscript{2}PtCl\textsubscript{6} \cdot 6H\textsubscript{2}O (Sigma-Aldrich);
- NAFION\textsuperscript{®} Perfluorinated resin solution 5 wt\% in mixture of lower aliphatic alcohols (2-propanol, n-propanol, methanol) and water contains 45\% water (Sigma-Aldrich);
- Sulphuric acid 99.999\%, H\textsubscript{2}SO\textsubscript{4} (Sigma-Aldrich);
- Perchloric acid 70\%, redistilled, 99.999\% metal basis, HClO\textsubscript{4} (Sigma-Aldrich);
- Compressed hydrogen gas (Air Liquide), H\textsubscript{2}, impurity: H\textsubscript{2}O < 3ppm; O\textsubscript{2} < 2ppm; CnHm < 0.5ppm;
- Compressed oxygen gas (Air Liquide), O\textsubscript{2}, impurity: H\textsubscript{2}O < 3ppm; CnHm < 0.5ppm;
- Compressed nitrogen gas (Air Liquide), N\textsubscript{2}, impurity: H\textsubscript{2}O < 3ppm; O\textsubscript{2} < 2ppm; CnHm < 0.5ppm;
- Compressed carbon monoxide gas (Air Liquide), CO, technically pure.
All reaction solutions and electrolytes were prepared with distilled water that was further purified with Millipore Milli-Q nanopure water of resistivity ≈ 17 M Ω cm. All the chemicals were of analytical grade purity and were used without further purification.

**Apparatus:**

- SEM experiments were performed with JEOL Model JSM-5400 scanning electron microscope equipped with a Shimadzu 800HS EDX.
- The XRD spectra were recorded on sample powders. X-ray diffraction (XRD) data were recorded using an automated PHILIPS diffractometer equipped with Soller slits and CuKα source (λ= 1.541 Å), 1° divergence-slits, 0.1 mm receiving slits a graphite diffracted-beam monochromator.
- The IR spectra of our samples were recorded in the ATR mode (Attenuated Total Reflectance), with PerkinElmer Spectrum 100 Series FT-IR spectrometer.
- UV-Visible spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer.
- The TEM imaging were done with Tem LEO 912AB instrument. (University of Milan)
- Electrochemical experiments were carried out with the CH Instruments (Austin, TX) model 832, in a Pine AKCELL3 three-electrode cell. The working electrode (RRDE) was a PINE special MT29 series tips with Glassy carbon Rings (collection efficiency: 37%; disk area: 0.2475 cm²) driven by a Pine rotator 636 ring-disk electrode system (Pine Instruments, USA). The reference electrode was K₂SO₄ saturated Hg/Hg₂SO₄ (MSE), and Pt flag as counter electrode. All the potentials are reported versus the standard hydrogen electrode (SHE). The MSE reference electrode was used to avoid possible contamination of chloride come from electrolyte solution. Two supporting electrolytes of 0.1 M HClO₄ and 0.5 M H₂SO₄ in ultra-pure water was used. All electrochemical analysis are made at 25°C with Haake F3-K Refrigerated Circulating Water Bath.
- A FC-05-02 5 cm² cell from Electrochem. Inc. controlled by a Scribner Associated 890CL fuel cell test system was used for the fuel cell experiments.

**Procedures:**

Salts (POMs) was prepared using the following steps. An aqueous solution of Cs₂CO₃ was added drop-wise to an PVM solution (in u.p. water) under vigorous stirring. The fine suspension was held at 30°C overnight and subsequently evaporated to dryness at 50°C. The ratio PVM–cesium carbonate was regulated to obtain the desired stoichiometry. When drying process is done, the product is ground in a mortar and weighed. Finally, the compound is stored in a 4cc vial, under vacuum desiccator.
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Pt-POMs by impregnation method it is similar to mixing method, but in this case we incorporate the catalyst (Pt) inside the catalytic support during the synthesis. Before adding the cesium salt, platinic acid is dropped into solution and subsequently evaporated and dried at 50°C. The product is stored and weighed in dry-box, due to its high hygroscopic property. Theoretically this kind of synthesis should be better than mixing method, because the Pt insertion occurring inside the support can allow a better dispersion and higher active catalyst area, differently to mixing method were the Pt is added after the synthesis, thus allowing only a superficial catalyst dispersion.

Some sample prepared by impregnation method was reduced using 5% H₂/Argon stream at 300°C.

For the Ink preparation with the salts prepared by mixing method, the procedure is to mix in a vial an amount of salt with Pt/Vulcan in 985 μl of isopropanol and sonicate for 10 seconds in a water bath. Only after, 15 μl of Nafion solution are added and put under stirring overnight. The weights of salt and Pt/Vulcan are calculated in...
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according to the Pt loading wanted on the electrode. In this thesis usually 10/15 μg Pt/cm² are deposited on electrode surface. The Pt/salt/ pure Nafion 1:1:1 mass ratio is used. Before the experiments, the working electrode is cleaned with Al₂O₃, with particle sizes of 0.05 μm. An amount of 7/4 μl of the prepared ink is deposited on the electrode surface trough a Hamilton 701n 10 μl syringe and let dry for 30 minutes in air. The electrolyte solution is degassed in N₂ for 30 minutes before every experiment. The activation process of catalytic layer consists in a 30 minutes of cyclic voltammetry at 50mV/s in nitrogen flux (until obtaining a stable voltammogram).

![Figure 6: ink preparation scheme by mixing method.](image)

In hydrogen oxidation reaction analysis before every test the system is saturated with Hydrogen for at least 30 minutes to reach a stable voltammogram. During the experiment the cell is kept in hydrogen atmosphere. A linear sweep voltammetry (LSV) is performed during the electrode rotation at 2500, 2000, 1600, 1200, 900, 600 and 400 rpm following the order. In the end a second control test is performed at 1600 rpm to check if there are any difference with the previous. Finally, LSV at 1600 rpm is made after 30 minutes of nitrogen flux to obtain the background current.

All ORR is made after HOR cycling at least 30 minutes in pure oxygen saturated solution, until a stable voltammogram is obtained. During the experiment the cell is kept in Oxygen atmosphere. A cyclic voltammetry (CV) is performed during the electrode rotation at 2500, 2000, 1600, 1200, 900, 600 and 400 rpm following the order. In the end a second control test is performed at 1600 rpm to check if there are any different with the previous. Finally a CV at 1600 rpm is made after 30 minutes of nitrogen flux to obtain the background current. Between each experiment a CV is performed until a stable voltammogram obtained. The temperature of the system is kept at 25ºC.

For CO striping voltammetry experiments, CO adsorption is performed by bubbling CO gas (technical purity 99%, Airgas) into a 0.1 M HClO₄ electrolyte for 5 minutes and 0.1V vs SHE applied for 200 seconds. The electrolyte solution is then purged with nitrogen gas (high purity 99.9%, Airgas) for 30 minutes to remove dissolved CO. Finally CO stripping is carried out by 4 cyclic voltammtries at 20 mv/s. All measurements are made at 25ºC.
Results and discussion:

The compounds synthesized in this work are shown below in Table 1:

Table 1: List of synthesized product.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Given Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs&lt;sub&gt;2.5&lt;/sub&gt;H&lt;sub&gt;1.5&lt;/sub&gt;PMo&lt;sub&gt;11&lt;/sub&gt;V&lt;sub&gt;1&lt;/sub&gt;O&lt;sub&gt;40&lt;/sub&gt;·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>POM 2.5-1-11</td>
</tr>
<tr>
<td>Cs&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;1&lt;/sub&gt;PMo&lt;sub&gt;11&lt;/sub&gt;V&lt;sub&gt;1&lt;/sub&gt;O&lt;sub&gt;40&lt;/sub&gt;·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>POM 3-1-11</td>
</tr>
<tr>
<td>Cs&lt;sub&gt;3.5&lt;/sub&gt;H&lt;sub&gt;0.5&lt;/sub&gt;PMo&lt;sub&gt;11&lt;/sub&gt;V&lt;sub&gt;1&lt;/sub&gt;O&lt;sub&gt;40&lt;/sub&gt;·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>POM 3.5-1-11</td>
</tr>
<tr>
<td>Cs&lt;sub&gt;2.5&lt;/sub&gt;H&lt;sub&gt;2.5&lt;/sub&gt;PMo&lt;sub&gt;10&lt;/sub&gt;V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;40&lt;/sub&gt;·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>POM 2.5-2-10</td>
</tr>
<tr>
<td>Cs&lt;sub&gt;3.5&lt;/sub&gt;H&lt;sub&gt;1.5&lt;/sub&gt;PMo&lt;sub&gt;10&lt;/sub&gt;V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;40&lt;/sub&gt;·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>POM 3.5-2-10</td>
</tr>
<tr>
<td>20%Pt-Cs&lt;sub&gt;2.5&lt;/sub&gt;H&lt;sub&gt;2.5&lt;/sub&gt;PMo&lt;sub&gt;10&lt;/sub&gt;V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;40&lt;/sub&gt;·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Pt-POM 2.5-2-10</td>
</tr>
<tr>
<td>20%Pt-Cs&lt;sub&gt;3&lt;/sub&gt;HPMo&lt;sub&gt;11&lt;/sub&gt;V&lt;sub&gt;1&lt;/sub&gt;O&lt;sub&gt;40&lt;/sub&gt;·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Pt-POM 3-1-11</td>
</tr>
<tr>
<td>20%Pt-Cs&lt;sub&gt;3.5&lt;/sub&gt;H&lt;sub&gt;2.5&lt;/sub&gt;PMo&lt;sub&gt;10&lt;/sub&gt;V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;40&lt;/sub&gt;·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Pt-POM 3.5-2-10</td>
</tr>
</tbody>
</table>

Each given name is based on the following rationale:

First abbreviation:
- POM = polyoxometalates
- Pt-POM = polyoxometalates were Pt is directly included by impregnation method synthesis

The numbers:
- 1<sup>st</sup> = Cesium stoichiometric number
- 2<sup>nd</sup> = Vanadium stoichiometric number
- 3<sup>rd</sup> = Molybdenum stoichiometric number

SEM analyses:

Figure 7 and Figure 8 show the micrographs of the starting HPAs in which arrays of crystals are observed.

![Figure 7: SEM images (from left: 500x and 2500x magnification) of PVM 1-11.](image)
The micrographs of Cs salts (prepared by mixing method) (Figure 9, Figure 10) show different types of agglomerates of small spherical nanocrystals grains that appear to be more dispersed in contrast with starting HPAs; this suggests a morphological modification after the reactions. POM 2.5-1-11, POM 3-1-11, POM 3.5-1-11, POM 2-1-11 appear to be bigger than POM 2.5-2-10 and POM 3.5-2-10.
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Figure 11, Figure 12 and Figure 13 shows the micrographs of Cs salts with Pt intercalated in the structure thanks to the impregnations synthesis. Different type of agglomerates of small nanocrystals are evident. The particles size from instrumental analyses results to be in a range of 100-500 nm. POMs synthesized with Impregnation method seem to form more uniform structure than the previous salts without Pt. Further studies are necessary to have a complete screen of all structure, so as select the more dispersed salts that should give the best results. Pt-POM 3-1-11 and Pt-POM 3.5-1-11 show a greater dispersion of the particles respect to Pt-POM 2.5-2-10, which remain more aggregated. After reduction process in Ar/H₂ at 300°C to form Pt particles before the electrochemical analysis, the morphologies of POMs are unchanged. Micrograph of backscattered electrons (BSE) was used to confirm the presence of fine Pt dispersion, but some large aggregates.

Figure 11: SEM images (5000 magnifications) of (a) Pt-POM 2.5-2-10, (b) Pt-POM 2.5-2-10 after reduction in Ar/H₂ and (c) Micrograph of BSE of Pt-POM 2.5-2-10 after reduction in Ar/H₂.

Figure 12: SEM image of: (a) Pt-POM 3-1-11 (10000x magnification); (b) Pt-POM 3-1-11 after reduction in Ar/H₂ (5000x magnification); (c) Micrograph of BSE of Pt-POM 3-1-11 after reduction in Ar/H₂ (5000x magnification).

Figure 13: SEM image of: (a) Pt-POM 3.5-1-11 (10000x magnification); (b) Pt-POM 3.5-1-11 after reduction in Ar/H₂ (5000x magnification); (c) Micrograph of BSE of Pt-POM 3.5-1-11 after reduction in Ar/H₂ (5000x magnification).
**IR analyses:**
The IR analysis shows the characteristic bands of Keggin structure\[^{x}\], in the region between 800-1200 cm\(^{-1}\).
The bands typical of the Keggin structure are:
- P-O bond Stretching at 1056 cm\(^{-1}\);
- Mo = O bond Stretching at 955 cm\(^{-1}\);
- Mo-O-Mo bond Stretching at 870 cm\(^{-1}\) and 730 cm\(^{-1}\).

**Figure 14** shows the IR spectra of PVM 1-11 and different POM salts. All compounds exhibit almost the same IR spectra, with pattern similar to starting PVM. The band at 741, 858, 955, 1058 cm\(^{-1}\) can be confidently attributed to Mo-O-Mo bridge stretching, Mo = O bond asymmetric stretching and P-O bond stretching of PO\(_4\) tetrahedron. There is a presence of shoulder peaks at 999 and 1075 cm\(^{-1}\) for the POMs samples. This asymmetry for P-O bond vibration (1058 cm\(^{-1}\)) and Mo = O bond asymmetric stretching (955 cm\(^{-1}\)) indicates the presence of Vanadium atom in the structure, that replace one or more Mo atoms. This is confirmed by literature that reported the stretching of V = O at 1070 cm\(^{-1}\).\[^{xii}\] The little shift of the IR salts values respect to starting PVM is related to the presence and distribution of Cs\(^{+}\) cation in the material.

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**HOR analyses:**
In all cases the solutions have been saturated 30 min with Hydrogen as long as a stable cyclic voltammetry has been reached. The experiments are carried out at 50mV/s in HClO\(_4\) 0.1M. All samples analysed in this chapter are made with a 1.1 Pt:POM mass ratio and a Pt loading of 15μg/cm\(^2\).
Figure 15: Cyclic voltammograms recorded in 0.1 M HClO₄ solution saturated with hydrogen. Scan rate, 50 mV/s.
Figure 15 shows the cyclic voltammograms of catalytic layers compared with the reference unmodified commercial ink. In the voltammograms the peaks of Cs salts cannot be distinguished due to overlapping with Hydrogen adsorption process on Pt in the region 0-0.3 V. A weak peak around 0.45V appears for the modified layer corresponding to the reduction of salts. The Cs salts peaks corresponding to the formation of Pt-oxo (PtO or PtOH) species tend to shift to more positive potentials respect to unmodified layer. This behaviour indicates a facilitate adsorption and activation of Hydrogen molecules during electrocatalysis.

Table 2: Comparison between Calculate active area and R factor of different POMs mixed with Pt/C 20%.

<table>
<thead>
<tr>
<th>INK</th>
<th>Calculate Active Area</th>
<th>Roughness Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C 20% ETEK + Vulcan XC-72R</td>
<td>2.240181 cm²</td>
<td>9.051236</td>
</tr>
<tr>
<td>Pt/C 20% + POM 3-1-11</td>
<td>2.461248 cm²</td>
<td>9.944435</td>
</tr>
<tr>
<td>Pt/C 20% + POM 3.5-1-11</td>
<td>2.333807 cm²</td>
<td>9.429524</td>
</tr>
<tr>
<td>Pt/C 20% + POM 2.5-2-10</td>
<td>2.516507 cm²</td>
<td>10.16771</td>
</tr>
</tbody>
</table>

The coulombic charge for hydrogen desorption was used for calculating the active Pt surface area by assuming that a stripping charge of 210 microcoulombs corresponds to hydrogen adsorption/desorption on 1 cm² of Pt area. As we can see from the Table 2 the calculated active area and the Roughness factor for POM's are higher than Pt/C 20% without catalysts. This can be translated in higher active surface that the modified layer has available for HOR. To better confirm the higher catalytic activity of the modified layers respect to commercial Pt/Vulcan XC-72R and evaluate electrocatalytic activity towards HOR, RDE voltammetric measurement have been performed.
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![Graph](image)

Figure 16: RDE voltammograms at 1600 rpm recorded in 0.1 M HClO₄ solution saturated with Hydrogen. Scan rate, 5 mV/s.

It is possible to see from the Figure 16 the limit currents that depend to reactant, assumes the same concentration of H₂ for all experiments, is higher for all inks modified with POMs respect to catalytic layer formed with commercial Pt/C 20%. This suggest that there are an increased dispersion of the catalytic centres and, thus higher active area. In the Table 2 the comparison between active area and Roughness factors for all layers are shown; the higher active area and Roughness factor for the inks prepared by mixing method respectively confirm that the Pt particles are more exposed in the modified layers.

**ORR analyses:**
After the HORs, the ORRs measurements have been performed. In all cases the solutions have been saturated 30 min with Oxygen as long as a stable cyclic voltammetry has been reached. The experiments are carried out at 50mV/s in HClO₄ 0.1M.
The limit current of inks modified with POMs are higher than commercial Pt/C 20%. Respect to the hydrogen, the ORR shows a high current respect, as for HOR, a higher surface area. In addition, in Figure 17 is possible to see a shift on ORR onset potential between commercial Pt/C 20% and modified layer having comparable Pt loading (15 μg/cm²). This shift indicates a lower activation energy due to a more favourable kinetics for the ORR. In all of case the wave of the composites is displaced at higher potential when compared with the reference catalyst. This testifies that the presence of insoluble salt in the INKs improves the catalytic activity of the Pt particles. Several factors such as porosity, surface area, Pt particles dispersion, H⁺ availability from POM matrix, amount of conductive agent may improve the catalytic activity. We can thus hypothesize better electrode performance in the case of real Fuel Cell.

**CO-Stripping analyses:**
The CO-stripping analysis is useful to analyse the dynamics of CO poisoning catalyst discovering the CO affinity that exist between CO and catalyst on a given support.
Table 3: Peak and Onset potential for CO oxidation adsorbed on the catalytic layer of different systems (pure Pt/C as a reference).

<table>
<thead>
<tr>
<th>INK</th>
<th>Peak Potential/V</th>
<th>Onset Potential/V</th>
<th>mol/cm$^2$ CO</th>
<th>g/cm$^2$ CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C 20% ETEK + Vulcan XC-72R</td>
<td>0.84</td>
<td>0.76</td>
<td>1.64E-08</td>
<td>4.62E-07</td>
</tr>
<tr>
<td>Pt/C 20% + POM 3-1-11</td>
<td>0.77</td>
<td>0.63</td>
<td>1.29E-08</td>
<td>3.62E-07</td>
</tr>
<tr>
<td>Pt/C 20% + POM 3.5-1-11</td>
<td>0.83</td>
<td>0.70</td>
<td>1.5E-08</td>
<td>4.2E-07</td>
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<tr>
<td>Pt/C 20% + POM 2.5-2-10</td>
<td>0.83</td>
<td>0.71</td>
<td>1.62E-08</td>
<td>4.55E-07</td>
</tr>
</tbody>
</table>

For all the catalytic layers, the CO adsorbed on Pt surface is completely oxidized in the first anodic scan, evident in the subsequent anodic scan where there are no peaks between 0.6 and 1 V, but is present the Hydrogen peak at 0V vs SHE (Figure 18). As shown in the Table 3 the Peak and Onset potential values of the systems modified with POMs are lower than for the reference system; the same improvement was observed relate to the calculated mole value and grams of CO stripped by the electrode surface. The results suggest that the CO stripping starts before for the system modified and the quantity of CO adsorbed is less than commercial Pt/C 20%. The Cs-POM salts could behave as redox mediator for the CO-oxidation reaction with the Pt present in the system. The proposed mechanism probably proceeds via the following reaction:

1. $\text{POM} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{POM}$
2. $\text{H}_2\text{POM} \rightarrow \text{HPA} + 2\text{H}^+ + 2\text{e}^-$

The catalytic enhancement of the layer with Cs salts containing HPA as matrix may be due to synergistic effect between Pt and POM.

All of these electrochemical tests (HOR, ORR, CO-stripp) were also performed with samples with different ratios of Pt/C 20%: POMs (1:1 and 1:2) with unsatisfactory results, and also with less Pt loading achieving good result.

Fuel Cell analyses:

Taking into account the physical characterization and the electrochemical analysis carried out previously, the salt Pt-POM 3-1-11 (impregnation method) has been choosen for the following Fuel Cell analyses. One electrode was a commercial ETEK (anode, $L_{\text{Pt}}$: 0.5 mg/cm$^2$) and the other was prepare using Pt-POM 3-1-11 (cathode, $L_{\text{Pt}}$: 0.44 mg/cm$^2$). The activation was achieved by feeding humidified gas, in our case hydrogen and oxygen, at the anode and cathode respectively. The cathode potential was brought in step down to 0.2V to obtain complete Pt$^{4+}$ reduction to Pt$^0$. At the end of these process that required about 4-5 h, the cell’s OCV reach a value of 0.96-0.97 V. Note that XX/YYZZ represent the Anode humidifier temperature / Cell temperature / Cathode humidifier temperature. In this chapter was analysed two different MEAs:
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- Comm. MEA = anode: Pt/C 20% ETEK 0.5 mg/cm$^2$; cathode: Pt/C 20% ETEK 0.5 mg/cm$^2$
- Mod. MEA = anode: Pt/C 20% ETEK 0.5 mg/cm$^2$; cathode: Pt-POM 3-1-11 0.44 mg/cm$^2$

Figure 19: Polarization and power curves of: Mod. MEA (anode: ETEK commercial 0.5 mg/cm$^2$; cathode: Pt-POM 3-1-11 0.44 mg/cm$^2$); Mod. MEA BIS (anode: Pt-POM 3-1-11 0.44 mg/cm$^2$; cathode: ETEK commercial 0.5 mg/cm$^2$), obtained with temperature of 70/70/70 ºC, feed gas H$_2$ 100ml/min, O$_2$ 200ml/min, 100% humidification, 2 bar.

The two polarization curves and the relative power curves in Figure 19 have been obtained by switching the feed gases without disarm the Fuel Cell (Mod. MEA before and Mod. MEA BIS after switched gases); in this way it is possible to use the cathode as anode and vice versa. Before changing from one feed gas to the other the cell was purged with nitrogen for at least 10–15 min following the safety instructions. As it may be seen the responses are about the same. This means that Pt loadings of the order of 0.44 mg/cm$^2$ are sufficient to realize an efficient catalyst for oxygen reduction and that the composite catalyst works well also for hydrogen oxidation. Is possible to notice a little power density loss after switching the gas; we can hypothesize that it is causes by degradation of the system due to the normal cell lifecycle. In Figure 20 there is a comparison of the data taken in Figure 19 with a fully commercial MEA (anode and cathode, L$\text{Pt}$: 0.5 mg/cm$^2$). The performance loss of about 50% and an increasing of Ohmic resistance are evident in the cell with anode or cathode POMs based. Remembering the elevated POMs hygroscopic properties mentioned earlier in this thesis, it’s easy to hypothesized that the power losses may be caused by a cell "flood" during the analysis. To confirm this hypothesis was carried out a further test with low RH:
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Figure 20: Polarization and power curves of: Comm. MEA (anode: Pt/C 20% ETEK 0.5 mg/cm²; cathode: Pt/C 20% ETEK 0.5 mg/cm²); Mod. MEA (anode: ETEK commercial 0.5 mg/cm²; cathode: Pt-POM 3-1-11 0.44 mg/cm²); Mod. MEA BIS (anode: Pt-POM 3-1-11 0.44 mg/cm²; cathode: ETEK commercial 0.5 mg/cm²). Results obtained with a temperature of 70/70/70 ºC, feed gas H₂ 100ml/min, O₂ 200ml/min, 100% humidification, 2 bar.

Figure 21: Polarization and power curves of: Comm. MEA (anode: ETEK commercial 0.5 mg/cm²; cathode: ETEK commercial 0.5 mg/cm²); Mod. MEA (anode: ETEK commercial 0.5 mg/cm²; cathode: Pt-POM 3-1-11 0.44 mg/cm²). Results obtained with a temperature of 40/70/40 ºC, feed gas H₂ 100ml/min, O₂ 200ml/min, 21% humidification, 2 bar.

The data in Figure 21 is a somewhat surprising result because we have obtained an outstanding improvement of catalytic activity of the Pt nanoparticles supported by insoluble POM respect to the commercial electrodes, confirming the hypothesis of cell flooding in the previous experiment. This test was performed with flow temperature of 40ºC for both fuels and cell temperature of 70ºC with a resulting RH of 21%.

Figure 22 shown that the resistance of POMs cell is lower than commercial cell probably due to a better diffusion of fuel gas inside the POMs electrode.
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Figure 22: Resistance curve comparison of: Comm. MEA (anode: ETEK commercial 0.5 mg/cm\(^2\); cathode: ETEK commercial 0.5 mg/cm\(^2\)); Mod. MEA (anode: ETEK commercial 0.5 mg/cm\(^2\); cathode: Pt-POM 3-1-11 0.44 mg/cm\(^2\)). Results obtained with a temperature of 40/70/40 °C, feed gas \(H_2\) 100ml/min, \(O_2\) 200ml/min, 21% humidification, 2 bar.

Figure 23: Open Circuit Potential comparison between: Comm. MEA (anode: ETEK commercial 0.5 mg/cm\(^2\); cathode: ETEK commercial 0.5 mg/cm\(^2\)); Mod. MEA (anode: ETEK commercial 0.5 mg/cm\(^2\); cathode: Pt-POM 3-1-11 0.44 mg/cm\(^2\)). Results obtained with a temperature of 40/70/40 °C, feed gas \(H_2\) 100ml/min, \(O_2\) 200ml/min, 21% humidification, 2 bar.

Finally in Figure 23 are reported the Open Circuit voltage, where the cell with POM modified electrode gives a higher potential of 0.037 V more than the fully commercial cell. These results are probably because the POM used, is able to retain the right amount of moisture inside the electrodes at lower relative humidity compared to the commercial electrodes (elevated POMs hygroscopic properties). This makes viable the use of simpler apparatuses for the gas control and energy savings in the fuel gas preheating. If we compared the Comm.MEA at RH 100% and Mod.MEA at RH 21%, the first have the best performance but the difference is not very high, so it is possible to think that the economical energy saving in apparatuses can compensate the little performance loss.
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Conclusions:

This work is focused on the development of proton highly conductive, mesomicroporous matrices for Pt catalysts and Pt-free catalysts that can be used to increase the catalytic performance and the CO tolerance of catalyst for PEMFC. The IR spectra performed clearly show that the primary Keggin structure of the heteropolyacids remains unaltered even when the protons are substituted by the Cs⁺ cations. This is important for the CO system tolerance that shall be attributed to the presence of molybdenum and vanadate units in the structure. The SEM micrographs presented clearly suggest that morphology of heteropolyacids changes deeply when the protons in heteropolyacid are substituted by Cs⁺ cations. The heteropolyacids surfaces are small crystals while the microstructure of Cs⁺ salts are small spherical nanocrystals grains that appear to be uniform. The electrochemical study of investigated materials has shown a better performance of electrode modified with POMs for HOR but especially for ORR, also, a lower Pt loading is allowed (15 to 10 μg/cm²) with a minimal loss of performance. Two likely hypotheses may be put forward to explain the reasons of the improvement of the catalytic activity (emerged from electrochemical tests) of the Pt nanoparticles supported by the insoluble mesoporous acid with respect to the standard catalyst. Due to the peculiar structure of the salt, the Pt nanoparticles trapped in the pores cannot grow above certain dimensions. This is the same concept exploited in organic catalysis where this type of salt are used as shape selective catalyst by regulating the dimensions of the pores to accommodate a particular reactants. The inclusion of the metallic particles in the POMs pores causes a decrease of the surface area and hence of the permeability of the gases. However, sufficient voids remain also in the case of the higher Pt content. This does not limit the transport properties of the catalytic layerxvi. Being mostly trapped the particles are less prone to be subject to aggregation phenomena. As regards the finals fuel cell analyses, is seen that the POMs allow a better cell performance at lower relative gas humidity, this makes possible the use of simplest apparatuses for the gas control and massive energy savings in the fuel gas preheating, without significant performance loss.

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