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Kinetic Study of Pt-H₃PMo₁₂O₄₀ for Methanol Electro-Oxidation

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ABSTRACT

Composite materials based on 30% wt of Pt dispersed on Vulcan carbon XC-72, using 5% wt of Nafion[®] ionomer and phosphomolybdic acid (H₃PMo₁₂O₄₀) were prepared for their application as co-catalyst for methanol electro-oxidation. Different amounts of H₃PMo₁₂O₄₀ were incorporated in order to determine the optimum amount to form the electrocatalytic layer. Composite materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman. The electrochemical characterization was carried out by cyclic voltammetry (CV) and impedance (EIS), using the composite materials over glassy carbon as working electrode, and solutions of 0.5M H₂SO₄ and 0.5M MeOH + 0.5M H₂SO₄ as electrolytes. Electrochemical results show that methanol oxidation is favored by the presence of H₃PMo₁₂O₄₀. Methanol electro-oxidation over-potential peak decreases around 150mV and a current increase of 50% is observed. These results open the opportunity to incorporate H₃PMo₁₂O₄₀ as part of the electrode-membrane assembly (MEA). However, this paper showed the first part, which was to determine the interaction between H₃PMo₁₂O₄₀ and Nafion. Further investigation will incorporate subsequently Pt into the composite for determine its kinetic parameters.

1 Introduction

Direct Methanol Fuel Cells (DMFCs) are part of the proposed technologies to achieve fewer emissions of gases such as CO_x , SO_x or NO_x that cause the greenhouse effect and related environmental problems. These devices use Pt as a catalyst, however, this metal is not abundant in the earth's crust (5×10^{-3} parts per million by weight). For this reason it is necessary to research new catalytic materials, which must be cheaper and have catalytic properties that allow a decrease in or the elimination of the Pt amount used and the achievement of the same or better activity on the reaction kinetics of electro-oxidation of methanol [1].

The polyoxometalates or heteropolyacids such as phosphomolybdic acid ($\text{PMo}_{12}\text{O}_{40}$) are rigid inorganic metal-oxygen compounds that are very strong Bronsted acids. Well known as high proton conductors, they exhibit fast reversible multi-electron redox behavior under mild conditions, and good stability in most of their redox states, which makes them attractive for applications in devices for electrochemical energy storage, such as DMFCs. The structure of the heteropolyacid choice consists of nearly spherical Keggin anions $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ of 12 Å diameter that are held together by an aqueous medium (Figure 1a). Keggin anion is illustrated in Figure 1b, and contains a phosphate group centered with four MoO_6 octahedral groups, each one sharing three edges. Each octahedron shares a pair of oxygen (O_p), and oxygen in phosphate group (O_{b2}) is bridged with other groups. Other Mo-oxygen bridges (O_{b1}) are shared by Mo atoms with bond length of ~ 1.65 Å to the terminal oxygen (O_t) to form poly-cations oxo-oxo-molybdenum ($\text{Mo} \equiv \text{O}_t$)⁴⁺ [2].

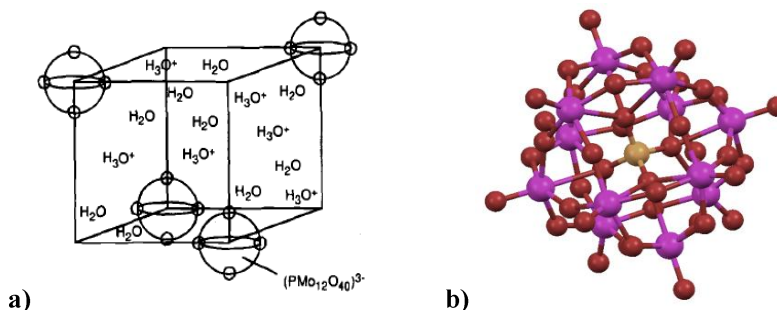


Figure 1.- Schematic representation of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot \text{H}_2\text{O}$ (a) and structure of Keggin anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (b).

A glassy carbon electrode was selected to be used as a substrate. Electron transfer kinetics is influenced significantly by pretreatment. This material could achieve negative potentials up to -1.0 V without significant evolution of hydrogen, common in aqueous media [3]. The potentiometric response of the carbon electrodes is influenced by the type and concentration of functional groups on the surface [4]. In other words, a carbon electrode that is immersed in an aqueous solution will acquire a potential, which will depend on the functional groups present on the carbon surface and their interaction with ions in solution. For this reason, it is known that carbon electrodes respond to redox

species in solution. The potentiometric response of carbon to ionic species in solution arises from the adsorption behavior of surface oxides. If the surface oxide has a quinone-type structure (C_xO), a positive electro kinetic potential is established by an equilibrium established between protons and anions (A^-) or cations (M^+) in solution:

(1)

A high acid concentration promotes the adsorption of protons in oxide-free sites (CxO) according to the following reaction:

(2)

In the above two reactions the anion is held in the diffuse double layer and is easily exchangeable with other anions in solution. The proton that attaches to the oxide group is strongly bound and must be neutralized by hydroxide, while the proton that is directly adsorbed on carbon is easily removed by washing with water. Studies of glassy carbon with Nafion coatings have been extensively reviewed by Natalya Yu [5]. These studies show that the Nafion acts as cation exchanger, so that negatively charged species do not show any reaction on the surface of glassy carbon. This implies that the sulfur (SO_3^-) groups of Nafion's own negative ions electrostatically repel other species in solution. In other words, the polymer is expected to act as a molecular sieve separator. This implies that the PMo_{12} would be repelled by a Nafion layer into the bulk of the solution. However, the low charge density of these anions allows us to imply that the electrostatic repulsion would be of low intensity.

In this context, this paper attempts to explain the interactions between the co-catalyst (PMo_{12}) and Nafion[®] ionómero as the first step toward obtaining kinetic parameters of the compound after the incorporation of Pt as catalyst. The electrochemical characterization of composite Nafion/ PMo_{12} /Pt are not showed, however, methanol oxidation is favored by the presence of $H_3PMo_{12}O_{40}$ and methanol electro-oxidation over-potential peak decreases around 150mV while a current increase of 50 % was observed.

2. Experiment

2.1. Composite GCE/Nafion and GCE/Nafion/ PMo_{12} preparation

For preparation of the working electrode, 5 μ L of Nafion ionomer (5 %wt) were place on the substrate surface (GCE/Nafion). Subsequently, in the case of the agglomerate Nafion/ PMo_{12} this was prepared as follows: 4 mg of PMo_{12} was dissolved in 1 mL of ethanol, then 5 μ L of this dilution was mixed with 5 μ L of Nafion, sonicating the resultant agglomerate for 5 minutes. Then, using a micropipette, 5 μ L of agglomerate was placed on freshly polished substrate allowed to dry for 10 minutes at room temperature.

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2.2. Electrochemical characterization

Electrochemical characterization of the different composites was carried out with a Biologic (Mod. XX) potentiostat-galvanostat in a conventional three-electrode cell. As reference electrode, Hg/Hg₂SO₄/K₂SO₄ (640 mV vs NHE) was used, and as counter electrode, Pt wire thin coiled. As substrate we used a glassy carbon electrode (BAS brand) with a geometric area of 0.0707 cm². Before placing the composites on the electrode, it was polished with alumina of different particle sizes (0.3 and 0.05 microns), subsequently rinsed with distilled water and sonicated for 10 minutes in methanol in order to remove any residual alumina that had remained on the surface.

Voltammetric studies were evaluated in two different equimolar solutions, one of acid medium and another of neutral medium: 1 mM [K₄Fe(CN)₆•3H₂O / K₃Fe(CN)₆] (hereinafter [Fe(CN)₆]^{3-/4-}) + 0.1 M H₂SO₄, and 1 mM [Fe(CN)₆]^{3-/4-} + 0.1M Na₂SO₄ both at room temperature (~ 25 °C), respectively. Before immersing the working electrode in the solutions, these were deoxygenated by bubbling N₂ gas (99.9% purity) for at least 10 minutes. It is important to clarify that all the voltammograms shown here are relative to the hydrogen electrode. The potential window considered for all experiments was 0.04 V to 1.04 V vs ENH, thus preventing the evolution of the medium in the form of H₂ and O₂ that could interfere with the reaction of interest.

3. Results and discussion

According to Noel and Anantharaman [6], the heat treatment of electrodes, which manufactures a glassy carbon, plays an important role in determining their surface properties. If an electrode is treated at high temperatures (from 600 to 3,000 °C), lower functional groups are formed on its surface and therefore, lower interactions with ions are present in solution. For our particular case, the work electrode that was used has two electrochemical signals very characteristic of this material, which are attributed to the quinone-hidroquinone pair as the inset showed in the Figure 1. This pair redox potential appears between 0.48 V and 0.60 V vs ENH.

In the same Figure 1, is shown the VC of the same work electrode (GCE), but now in the presence of the probe molecule [Fe(CN)₆]^{3-/4-}. The profile resembles that of [Fe(CN)₆]^{3-/4-}. However, potential peaks are shifted about 200 mV as reported in the literature [7], and which may be due to the acidic solution.

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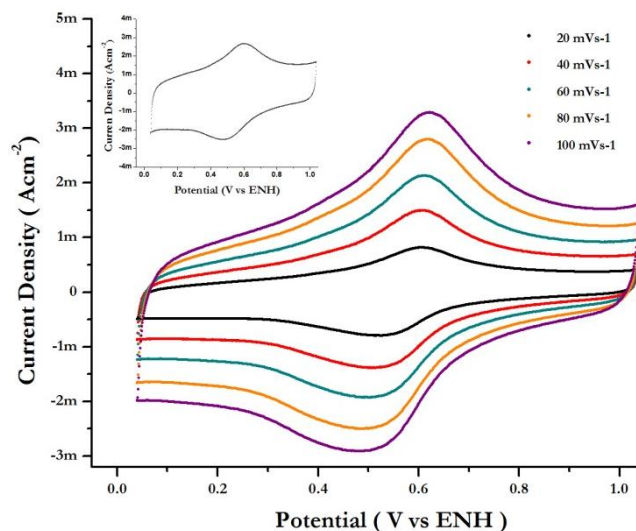


Figure 1. Cyclic voltammograms of the bare GC electrode in $[\text{Fe}(\text{CN})_6]^{3-/4-} + 0.1\text{M H}_2\text{SO}_4$ solution at different sweep rates, and inset: bare GCE in $0.1\text{M H}_2\text{SO}_4$ solution only at sweep rate of 100 mVs^{-1} .

As shown in Table 1, the trend shows the potentials (lowest to highest sweep rate) is similar at the peak potential of the quinone-hydroquinone pair as was obtained in the Figure 1 inset, which indicates that the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair in the presence of H_2SO_4 competes with the redox couple displaying the glassy carbon. For other hand, the current density increased due to the presence of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair, compared with Figure 1 inset.

Table 1. Potential of the anodic and cathodic peak of the GCE in $1\text{mM } [\text{Fe}(\text{CN})_6]^{3-/4-} + 0.1\text{M H}_2\text{SO}_4$ at different sweep rates. E_p [=] mV; $\Delta E_p = E_{p,a} - E_{p,c}$ and i_p [=] mA cm^{-2} .

Scan Rate (mVs^{-1})	$E_{p,a}$	$i_{p,a}$	$E_{p,c}$	$i_{p,c}$	ΔE_p
20	606	0.816	525	-0.80	81
40	607	1.5	507	-1.39	100
60	612	2.13	499	-1.93	113
80	615	2.8	486	-2.50	129
100	622	3.29	482	-2.92	140

Furthermore, Figure 2a shows the cyclic voltammogram of glassy carbon electrode with Nafion agglomerate (GCE/Nafion) in the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution and displays the same peaks as in Figure 1, which are close to the potential of the quinone-hydroquinone pair (see Table 2). However, the current densities again decrease, which can be attributed to the presence of Nafion on the electrode.

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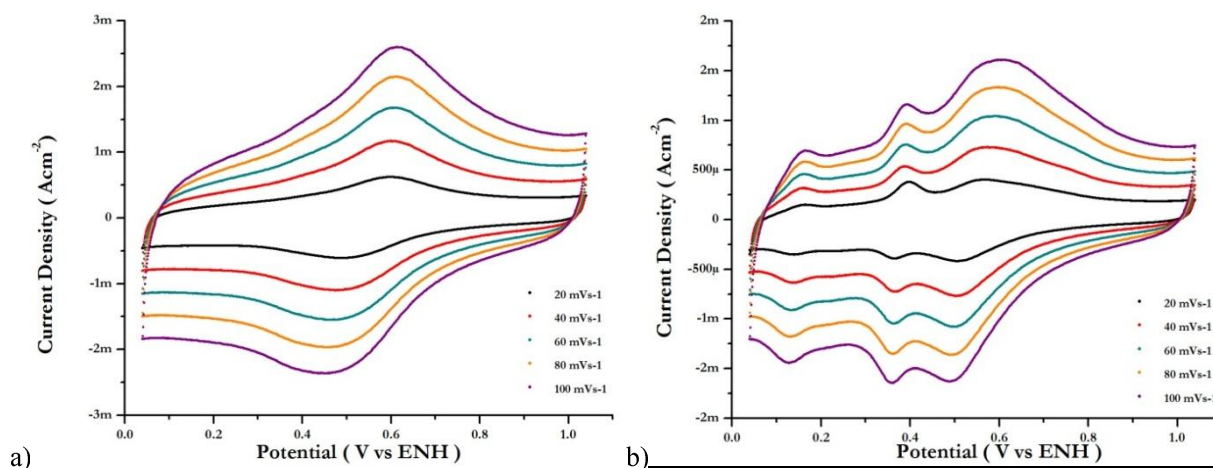


Figure 2. Cyclic voltammograms of the electrode GC/Nafion (a) and GCE/Nafion/PMo₁₂ (b) in [Fe(CN)₆]^{3-/4-} + 0.1M H₂SO₄ solution at different sweep rates.

It's important to remember that the Nafion functions as a selective molecular sieve which only allows the passage of protons across their micelles, so that the [Fe(CN)₆]^{3-/4-} pair is unable to reach the electrode surface to transfer its load. Therefore, no electrochemical responses are observed corresponding to the [Fe(CN)₆]^{3-/4-} pair, attributing the peaks that appear to the quinone-hydroquinone pair. On the other hand, the currents shown in Table 1 are greater than those in Table 2, which is attributed to the fact that the [Fe(CN)₆]^{3-/4-} pair in solution increases the capacitance of the electrode when not placed Nafion on the surface.

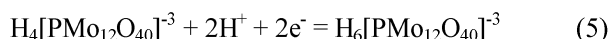
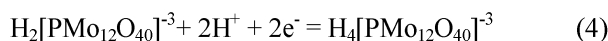
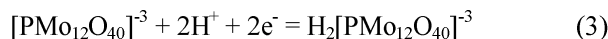
Table 2. Potential of the anodic and cathodic peak of the electrode GCE/Nafion in 1mM [Fe(CN)₆]^{3-/4-} + 0.1M H₂SO₄ at different sweep rates. E_p [=] mV; ΔE_p=E_{p,a}-E_{p,c} and I_p [=] mA cm⁻².

Scan Rate (mVs ⁻¹)	E _{p,a}	i _{p,a}	E _{p,c}	i _{p,c}	ΔE _p
20	597	0.623	488	-0.611	109
40	600	1.17	482	-1.10	118
60	609	1.68	474	-1.55	135
80	612	2.15	460	-1.97	152
100	613	2.60	449	-2.37	164

Thus according to the values of ΔE with respect to the sweep rate of Table 1 and 2, both systems (GCE and GCE/Nafion) behave quasi reversibly and irreversible, respectively, since ΔE increases as the sweep rate in the range of 75 to 165 mV.

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Figure 2b show the cyclic voltammogram of the GCE/Nafion/PMo₁₂ where one can see the appearance of peaks, which are attributed to the oxidation states of PMo₁₂ according to the following reactions [8]:



In Table 3, it can be seen that the peak that arises from PMo₁₂ overlaps with the peak corresponding to the quinone-hydroquinone pair reported above. In an acidic medium there is no signal corresponding to the [Fe(CN)₆]^{3-/4-} pair. However, it can be seen very clearly that it corresponds to PMo₁₂. On the other hand, it is to be noted that the capacitance of the electrode containing Nafion/PMo₁₂ is smaller than obtained with and without Nafion. Likewise, note that the current density of peaks in the direction of reduction are decreasing which is attributed to the different changes of oxidation states of PMo₁₂.

Table 3. Potential of the anodic and cathodic peak of the electrode GCE/Nafion/PMo₁₂ in 1mM [Fe(CN)₆]^{3-/4-} + 0.1M H₂SO₄ at different sweep rates. E_p [=] mV; ΔE_p=E_{p,a}-E_{p,c} and I_p [=] mA cm⁻².

	1st. Peak				2nd. Peak				3hr. Peak			
Scan Rate (mVs ⁻¹)	E _{p,a1}	i _{p,a1}	E _{p,c1}	i _{p,c1}	E _{p,a2}	i _{p,a2}	E _{p,c2}	i _{p,c2}	E _{p,a3}	i _{p,a3}	E _{p,c3}	i _{p,c3}
20	566	0.40	504	-0.42	398	0.38	364	-0.32	164	0.15	140	-0.35
40	575	0.73	503	-0.77	388	0.54	365	-0.73	158	0.32	143	-0.64
60	588	1.40	499	-1.08	390	0.76	363	-1.05	166	0.46	135	-0.91
80	601	1.33	500	-1.36	390	0.96	361	-1.35	165	0.58	129	-1.18
100	613	1.61	488	-1.63	393	1.16	358	-1.65	165	0.70	128	-1.44

Below are shown the results obtained based on the same methodology described above, but now in basic medium, for which 0.1M Na₂SO₄ solution was used as a supporting electrolyte. Figure 3 inset shows the VC glassy carbon electrode in the presence of the support electrolyte only. One can see that the quinone-hydroquinone peaks (seen in the first experiment, Figure 1) do not appear, which is attributed to the basic character of the supporting electrolyte. Recall that this redox couple is the result of a protonation of the functional groups found on the surface of the substrate.

Moreover, Figure 3 shows the cyclic voltammogram of the GCE immersed in the solution of the [Fe(CN)₆]^{3-/4-} pair with the supporting electrolyte which is similar to that reported in Figure 1. However, both anode and cathode potential peaks are displaced. In accordance with the values of Table 4, at a scan rate of 20mVs⁻¹, an anodic peak appears at a potential of 484 mV (basic medium). While in this acid environment a 606 mV peak appears, which

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gives a displacement relative to each other of 122 mV, a difference which is maintained constant regardless of the sweep rate at which each of the VC's has been performed.

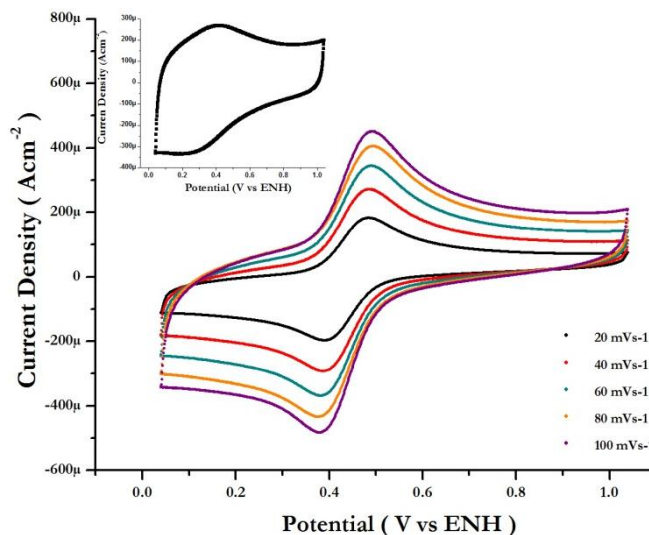


Figure 3. Cyclic voltammograms of the bare GC electrode in $[\text{Fe}(\text{CN})_6]^{3-/4-} + 0.1\text{M Na}_2\text{SO}_4$ solution at different sweep rates, and inset, bare GC electrode in $0.1\text{M Na}_2\text{SO}_4$ solution only, sweep rate: 100 mVs^{-1} .

Table 4. Potential of the anodic and cathodic peak of the GC electrode in $1\text{mM} [\text{Fe}(\text{CN})_6]^{3-/4-} + 0.1\text{M Na}_2\text{SO}_4$ at different sweep rates. E_p [=] mV; $\Delta E_p = E_{p,a} - E_{p,c}$ and I_p [=] mA cm^{-2} .

Scan Rate (mVs^{-1})	$E_{p,a}$	$i_{p,a}$	$E_{p,c}$	$i_{p,c}$	ΔE_p
20	484	0.183	391	-0.197	93
40	485	0.272	387	-0.292	98
60	490	0.344	383	-0.368	107
80	494	0.405	376	-0.434	118
100	493	0.451	378	-0.483	115

According to Figure 4a, by placing on the glassy carbon electrode a thin layer of Nafion does not allow the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair to approach the electrode surface to transfer electron. Therefore no signal in the voltammogram is seen. This behavior is consistent since, as a proton driver, the Nafion hinders the access of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair. However, this behavior changed when the GC/Nafion/ PMo_{12} electrode was immersed in the solution. Figure 4b show the voltammogram of the electrode mentioned above and suggests that the surface of the substrate is conducting an electronic transfer despite $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and PMo_{12} are negatively being charged. Table 5 summarizes the potential of anodic and cathodic peaks obtained from these voltammograms. As can be seen when comparing the peak potential of Table 4 and 5, there is a displacement of approximately 30 mV relative to each other. It can be said that the system of quasi-reversible steps is irreversible, as shown in Figure 4b.

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One possible reason proposed to explain the above behaviors is the fact that the $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ content in the agglomerate, by electrostatic repulsion between anion and sulfonic groups of the Nafion, increases the pore size through which the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ can access the electrode surface, so that, transferring the load gives rise to signals. However, the diffusion process is complicated, as voltammogram quasi-reversible to irreversible occurs.

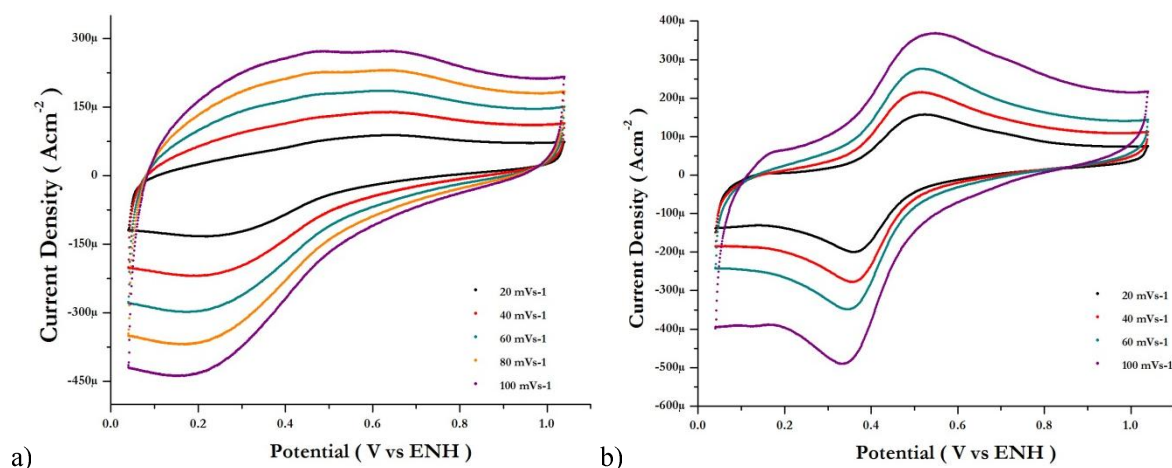


Figure 4. Cyclic voltammograms of the electrode GCE/Nafion (a) and GCE/Nafion/PMo₁₂ (b) in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ + 0.1M Na₂SO₄ solution at different sweep rates.

Furthermore it is likely that the protons (H^+), which are part of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ like against load, neutralize sulfonic groups (SO_4^- of Nafion) such that charge density decreases sufficiently to allow the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair thus close enough to transfer its load.

Table 5. Potential of the anodic and cathodic peak of the electrode GCE/Nafion/PMo₁₂ in 1mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ + 0.1M Na₂SO₄ at different sweep rates. E_p [=] mV; $\Delta E_p = E_{p,a} - E_{p,c}$ and I_p [=] mA cm⁻².

Scan Rate (mVs ⁻¹)	$E_{p,a}$	$i_{p,a}$	$E_{p,c}$	$i_{p,c}$	ΔE_p
20	524	0.157	361	-0.200	163
40	515	0.215	359	-0.278	156
60	519	0.276	346	-0.349	173
100	547	0.368	334	-0.491	213

4. Conclusions

In acid medium the GCE shows the quinone-hydroquinone pair is characteristic of materials regardless of the presence of a $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair. This pair remains consistent even after placing the electrode surface on the Nafion ionómero. This makes it clear that the observed peaks correspond to the quinone-hydroquinone redox couple, as the

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Nafion does not allow the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ to approach the electrode surface, only slightly increasing the capacitance of the electrode. The GC/Nafion/ PMo_{12} electrode shows the characteristic signals of the latter compound corresponding to the change in oxidation state of Mo contained within the anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ as a result of protonation.

Furthermore, in a neutral medium, CGE shows no peak characteristic of the pair corresponding to quinone-hydroquinone, which is attributed to the neutrality of the solution. In the presence of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair the voltammogram shows only the presence of the characteristic peaks of the pair, which are displaced approximately 200 mV with respect to the results obtained in acidic medium. The GC/Nafion electrode does not show the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ peaks, attributed to the fact that Nafion only allows the passage of protons, but not the anion, and is repelled by electrostatic forces to the bulk of the solution. When placing the composite over the Nafion/ PMo_{12} electrode, $[\text{Fe}(\text{CN})_6]^{3-/4-}$ peaks reappear, which is attributed to the increase in the agglomerate PMo_{12} , by electrostatic repulsion with SO_4^- groups. The pore size of Nafion allows the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair sufficient to approach the electrode surface to transfer its load. Also, the H^+ that contains the PMo as counter ions helps to neutralize the negative charges of Nafion to reduce the repulsive forces between SO_4^- and the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ pair. This study was conducted as part of a project aimed at determining the kinetic parameters that were initially proposed. This opens the possibility of improving the electro-active area of MEA's used in methanol fuel cells.

5. Acknowledgements

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6. References

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