Short communication

CO-tolerant electrodes developed with PhosphoMolybdic Acid for Polymer Electrolyte Fuel Cell (PEFCs) application

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Abstract

Several approaches were used to improve the CO-tolerant electrodes for polymer electrolyte fuel cells (PEFCs) when using processed H_2 as a fuel. The employment of transition metals oxides (WO_x, MoO_x) promotes CO oxidation and, for this reason, heteropolyacids (like PWA, PMoA, SiWA, etc.) containing these oxides were selected in this work, for the development of CO-tolerant electrodes.

Different electrodes were prepared by using a spray technique for both diffusive and catalytic layers. The catalytic layer was obtained using a 30 wt.% Pt/Vulcan as an electro-catalyst mixed with a Nafion solution for the standard electrode (SE).

CO-tolerant electrodes were prepared by adding different weight percentages (6–15%) of phosphomolybdic acid (PMoA) to SE and for all the prepared electrodes, the Pt loading was maintained as a constant at $0.5\,mg\,cm^{-2}$. Membrane electrode assemblies (MEAs) were obtained with an SE as a cathode and the electrodes containing different amounts of PMoA as anodes. A commercial N115 membrane was used as an electrolyte. MEAs were tested at $80\,°C$ in H_2/air and in H_2–CO (100 ppm)/air, in order to evaluate the performance loss in these operative conditions. By feeding the fuel cell (FC) with H_2–CO/air, an improvement in the cell performance proportional to the increase of the percentage of PMoA was observed.

The best value was reached by using a percentage of inorganic compounds in the range of 12–15 wt.%. A power density of about $240\,mW\,cm^{-2}$ at 0.6 V was obtained independently on the used fuel. A short time-test (160 h) was carried out at $80\,°C$ in H_2–CO/air with an average power density of $220\,mW\,cm^{-2}$, confirming the stability of the system. The right compromise between the Pt catalyst and the heteropolyacid ratio could be a helpful tool in limiting Pt poisoning.
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1. Introduction

Polymer electrolyte fuel cells are efficient electrical generators based on the electrochemical oxidation of hydrogen by oxygen. Both electrochemical reactions require catalysts, such as Pt to operate at a useful rate. In any case, the catalyst is poisoned by CO traces, when the cells are fed by H_2 obtained from the reforming of alcohols or hydrocarbons. For this reason, many efforts were made to improve the PEFC performance when reformed H_2 is used as a fuel, and different approaches were used to improve the CO tolerance of electrodes.

The most common approaches used for this aim are the replacement of the Pt catalysts, at the anode side, by Pt–M alloys;

the increase of the working temperature until $T = 150\,°C$; the introduction of small amounts of air mixed with the fuel at the anode side.

Several authors [1–4] report the use of binary Pt–Mo alloys as an anodic catalyst for CO tolerance. The use of molybdenum is interesting because it is a transition metal which is not expensive and is readily available. The presence of an additional element promotes the electro-oxidation of CO to CO_2 through a process involving OH^- species formed on the oxophilic sites on CO absorbed in the Pt sites (bifunctional mechanism). Moreover, the presence of another element can weaken the Pt–CO bond due to an electronic effect. This behaviour is attributed to Mo, mainly due to the oxygenated species of molybdenum (such as $MoO(OH)_2$) [5]. In fact, these species catalyse the water–gas shift reaction [6–9] and for this reason Mo does not show a good improvement when direct methanol is used as a fuel (DMFC). The same authors report the

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catalytic enhancement of CO oxidation on Pt by the addition of MoO_x, WO_x, etc., in the catalytic layer [10,11].

The corresponding heteropolyacid of Mo presents the Kegging structure, in which MO_x (M = W, Mo, etc.) octahedral surrounds a central XO_4 (X = P, As, Zr, etc.) tetrahedron. In addition, the heteropolymolybdates (PMoA) are strong oxidizing agents and in fact, are often used to catalyse the oxidation of hydrocarbon compounds [12]. In this work, our attention has been focused on the development of CO tolerant anodes for PEFC application by using a PMoA in the catalytic layer, to promote CO oxidation when reformed H_2 is used. Several anodes were prepared by adding different amounts (0–15%, w/w) of PMoA in the catalytic layer, and compared to home made standard electrodes (SE) with a Pt loading of $0.5\,mg\,cm^{-2}$ in a PEFC fed by H_2/air and H_2–CO (100 ppm)/air at $80\,°C$ (100% RH). An improvement in H_2–CO/air electrochemical performance, proportional to the PMoA percentage increase was observed.

2. Experimental

2.1. Electrodes and MEAs preparation

The electrodes were prepared by a CNR-ITAE spray technique [13] on carbon cloth (Textron) substrate. A diffusion layer (GDL) of Shanwiningan Acetylene Black (Chevron) and 50% (w/w) of PTFE was sprayed on carbon cloth and heat-treated at $350\,°C$. The catalytic layer was obtained by spraying a 30% (w/w) Pt/Vulcan (E-TEK) catalyst mixed with a Nafion solution (Aldrich, 5%, w/w), ammonium carbonate (Carlo Erba), and water on GDL [14]. The electrodes were dried at $150\,°C$. The Pt loading was maintained as a constant at $0.5\,mg\,cm^{-2}$ for all the prepared electrodes. A standard electrode (SE), prepared as described above, was used as a cathode for all the tested MEAs. The same preparation procedure was used for the catalytic layer of the anodes by mixing a different amount of phosphomolybdic acid $(H_3[P(Mo_3O_{10})_4]\cdot xH_2O$, Aldrich) with the slurry. In Table 1, the anodes composition is reported.

MEAs were obtained by hot pressing the electrodes at $130\,°C$ for 3 min on a commercial Nafion 115 membrane, previously purified in a 5 vol.% H_2O_2 solution (Carlo Erba) and in a 1 M H_2SO_4 solution (Carlo Erba).

2.2. Electrochemical characterisation

The electrochemical tests were carried out in a $5\,cm^2$ commercial single cell (GlobeTech) connected to a fuel cell test station. The measurements were performed at $80\,°C$ in H_2/air and in H_2–CO (100 ppm)/air. Gas pressures of 3 abs. bar were used with a constant gas flux of 1.5 and 2 times the stoichiometric value at $1\,A\,cm^{-2}$ for hydrogen and air, respectively. A relative humidity (RH, %) of 100% was fixed for both reactant gases. The polarisation curves were recorded with a test station equipped with a software for the data automatic acquisition and the cell resistance was measured with an Agilent milliohmmeter by a static method at a frequency of 1 kHz.

The time-test was carried out at a constant value of cell potential (0.4–0.5 V) recording the current density variation as a function of time with intervals of about 900 s for about 160 h.

The cyclic voltammetry and CO stripping were conducted at $80\,°C$ on the prepared electrodes (SE and PME15), by using the same housing and test station of I–V tests and a potentiostat–galvanostat (Autolab mod. PGSTAT30). In these experiments, the cathode was fed with H_2 and used as counter and reference electrode (HRE), while the anode was fed with N_2 and H_2–CO (2%) and used as working electrode. The voltammograms were obtained in the potential range between 0.1 and 1.2 V at a scan rate of $20\,mV\,s^{-1}$. The CO stripping was carried out after feeding the anode with H_2–CO mixture for 30 min at 0.1 V and successively by purging with N_2 for 1 h to remove the excess of CO.

2.3. EDX mapping

EDX mapping on the electrodes was performed by using a field emission scanning electron microscope equipped with an EDAX microprobe. Molybdenum, fluorine and platinum were mapped by utilising the L, K and K lines, respectively. The mapped surface is of about $20\,\mu m \times 10\,\mu m$ and the used mapping matrix had a dimension of 256×200.

2.4. Solubility test

A separated test of solubility was carried out to check if the PMoA absorbed onto the catalyst was not eluted from the water during the cell operation. Ink was prepared by using the Vulcan XC-72R (CABOT) and PMoA with the same ratio used in the electrode preparation (PME15) that supplied the best result. An amount of 1 g of PMoA was solubilised in 50 ml of distilled water and 4 g of carbon was added to the solution. The obtained dispersion was sonicated for about 15 min and desiccated in oven at $T = 80\,°C$ until complete dried. The powder was milled by a mortar and underwent XRD measurements.

A solubility test was carried out by treating about 1 g of the prepared mixture in 100 ml of distilled water at $T = 80\,°C$ under magnetic stirring for about 3 h. The dispersion was filtered (by using two Whatmann-542 filters), washed and desiccated for 20 h in an oven at $80\,°C$ and characterised by XRD measurements.

2.5. Powder X-ray analysis

The X-ray powder diffraction (XRD) analysis was performed using a Philips X-ray automated diffractometer (model

Table 1
Characteristics of the developed electrodes

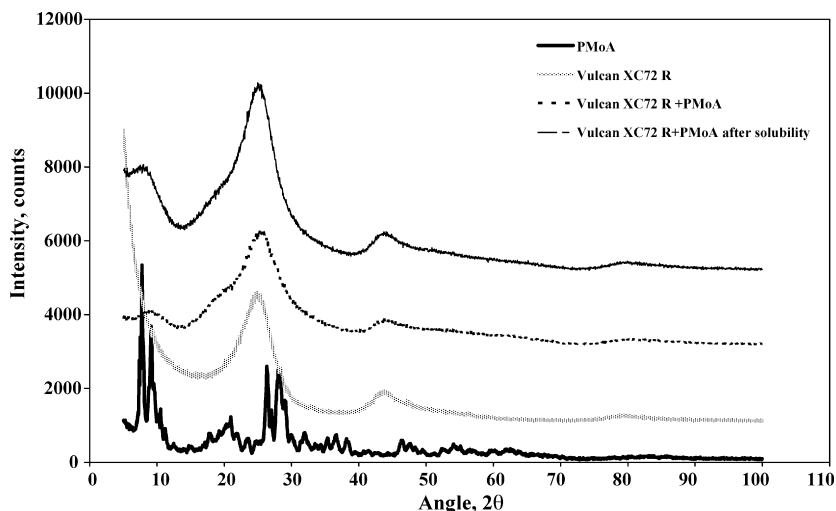| Anodes	% Catalyst	% Nafion	% PMoA
SE	67	33	0
PME6	63	31	6
PME9	61	30	9
PME12	59	29	12
PME15	57	28	15

Fig. 1. X-ray diffraction (XRD) analysis on the impregnated powder before and after the solubility test, compared to the commercial PMoA and Vulcan XC-72R.

PW3710) with Cu Kα radiation source. The 2θ Bragg angles were scanned between 5 and 100°.

3. Results and discussion

At first, to verify if PMoA was really adsorbed on the catalytic layer and not eluted from the water during the fuel cell operation, the carbon was impregnated as described in the solubility test section and characterised by XRD analyses before and after the solubility test.

In Fig. 1, the XRD profiles of the untreated PMoA, the untreated Vulcan XC-72R and the impregnated carbon before and after the solubility test are compared.

A crystalline structure of PMoA, with the main peaks centred at about 8.5, 25 and 29° 2θ and a broad signal at about 20° 2θ is evident. On the contrary, the XRD pattern of Vulcan XC-72R, does not present a typical crystalline structure, in fact at about 25 and 45° 2θ it is possible to observe two broadened peaks and the former of these presents a higher intensity than the latter. In the impregnated untreated carbon XRD profile, the peaks at 25

and 45° 2θ typical of the carbon are present, even if the peak at 25° is strongly broadened, which is attributable to the presence of the PMoA (peak at ∼20° 2θ). More evidence of the PMoA presence is highlighted by the broad peak at ∼8.5° 2θ related to the fundamental peak of the PMoA. This evidence is also confirmed in the profile of treated impregnated carbon. In fact, after the solubility test, the peak centred at 8.5° 2θ is still present and more intense, probably due to the elimination of some impurities related to the preparation procedure. Moreover, the enlargement of the peak at 25° 2θ is still maintained by supplying a further confirmation of PMoA stability in the electrodes.

The electrochemical characterisations in terms of current density–voltage curves, in both pure H_2/air and H_2–CO (100 ppm)/air were carried out for all the prepared MEAs. The standard cathode–anode couple (SE) was used as a reference. Moreover, the same standard electrode (SE) was used as a cathode and assembled at the different modified anodes. In Fig. 2 the polarisation curves in H_2/air are reported.

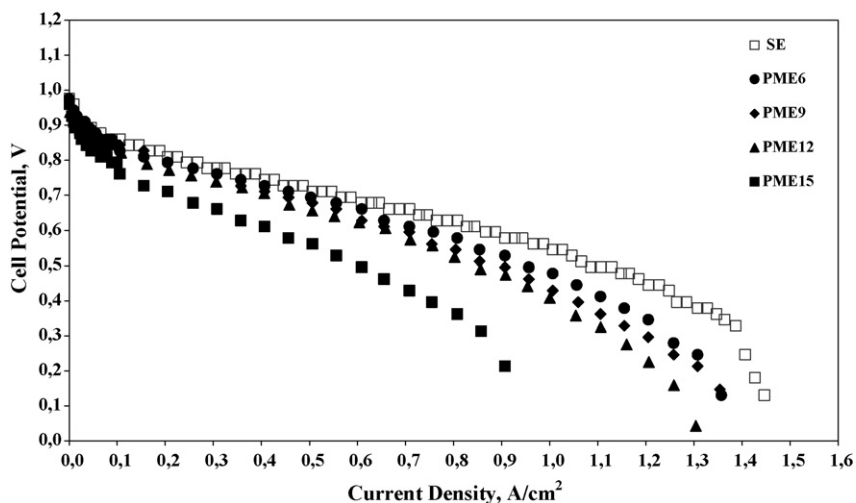The SE MEA presents the best performance in the full range of current density.

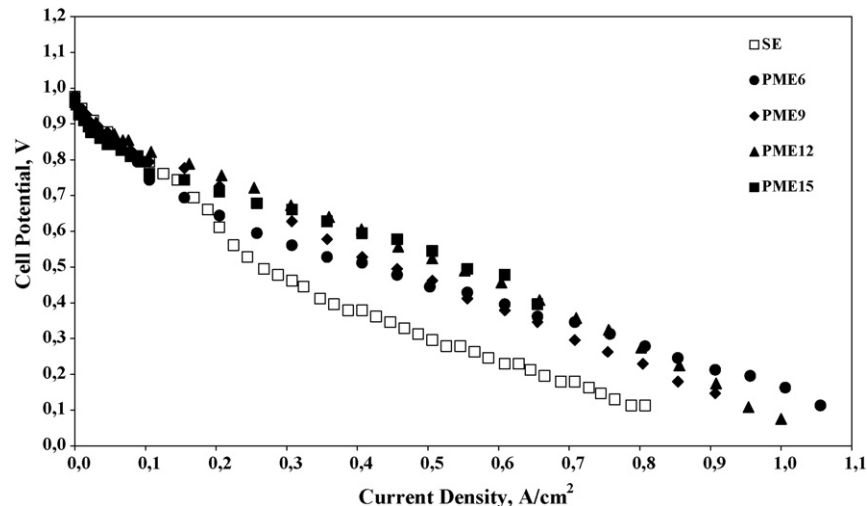Fig. 2. Polarisation curves of developed electrodes in H_2/air at 80 °C.

Fig. 3. Polarisation curves of developed electrodes in H_2–CO (100 ppm)/air at 80 °C.

The introduction of different percentages of PMoA into the catalytic layer produces a decrease in the performance proportional to the amount of heteropolyacid added.

In particular, the PME6, PME9 and PME12 MEAs, with 6, 9 and 12% of inorganic compound, respectively, show similar behaviour to SE in the activation and ohmic region of the polarisation curve, while in the diffusive region a proportional decrement is noticeable. In fact, a reduction in the limiting current is recorded from 1400 to 1300 mA cm^{-2}, probably due to mass transport problems related to the presence of PMoA that could limit the gas diffusion in reaching catalytic sites. This effect is more dramatic in the PME15 MEA, where a different behaviour in the whole range of current density of polarisation curve is observable. In this case a potential loss of about 27% compared to the SE MEA is recorded.

To verify the CO tolerance of the developed electrodes, all MEAs were tested in H_2–CO (100 ppm)/air. The *I–V* curves obtained are reported in Fig. 3.

As expected, the SE MEA shows the highest performance loss starting with the activation zone and influencing all the remaining parts of the polarisation curve. On the contrary, the modified electrodes exhibit a limiting current behaviour different from the classical pattern that clearly indicates a different oxidation mechanism in the mixed H_2/CO environment. Moreover, the performance improves proportionally with the amount of PMoA.

A confirmation of this behaviour is highlighted in Fig. 4, where the Tafel slope values as a function of PMoA percentages are reported for both the fuels used.

In the H_2 fed cell, an increase of the Tafel slope by increasing of the PMoA content is noticeable, thus, meaning a worse catalytic activity. In contrast, in the H_2–CO fed cell a decreasing of the Tafel slope is found with the increase of the PMoA content, thus, meaning a better catalytic activity compared to the CO oxidation.

An additive contribution of the PMoA presence is also found in the limiting current, meaning that the introduction of the inorganic compound does not interfere with the gas diffusion and the water management of the electrode. In particular, the presence of PMoA is limiting in the Pt distribution of the electrode when neat H_2 is used, because a partial coverage of Pt sites could be occupied. On the contrary, this distribution could be positive when the H_2–CO is used as a fuel, since the vicinity of two different catalysts permits a better Pt utilisation due to the CO oxidation of the Mo neighbouring. In order to verify this behaviour, CO stripping measurements were carried out on both SE and PME15 electrodes (Fig. 5).

In the SE cyclic voltammogram in the presence of CO, a typical peak due to the oxidation process of CO adsorbed on Pt sites, is present at 0.62 V. This peak disappears when the electrode was purged with N_2. From this voltammogram, the electrochemical Pt catalyst surface area (ECSA) was determined by integrating the area of the CO oxidation process peak, assuming 420 μC cm$^{-2}_{Pt}$ as a correcting factor to convert the charges to the Pt surface area. A value of about 80 m^2 g^{-1} is obtained.

Fig. 5 also reports the CV with and without CO for the PME15 electrode. In this case a well-defined peak at about 0.45 V is attributable to the Mo(IV) → Mo(VI) redox process, which is
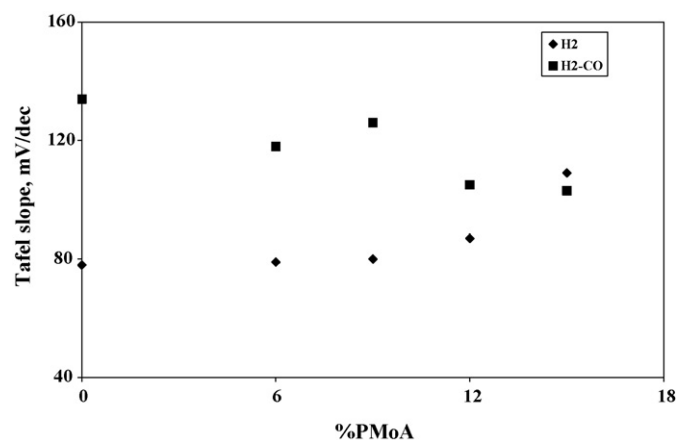

Fig. 4. Tafel slope dependence vs. PMoA % in H_2/air and H_2–CO (100 ppm)/air at 80 °C.
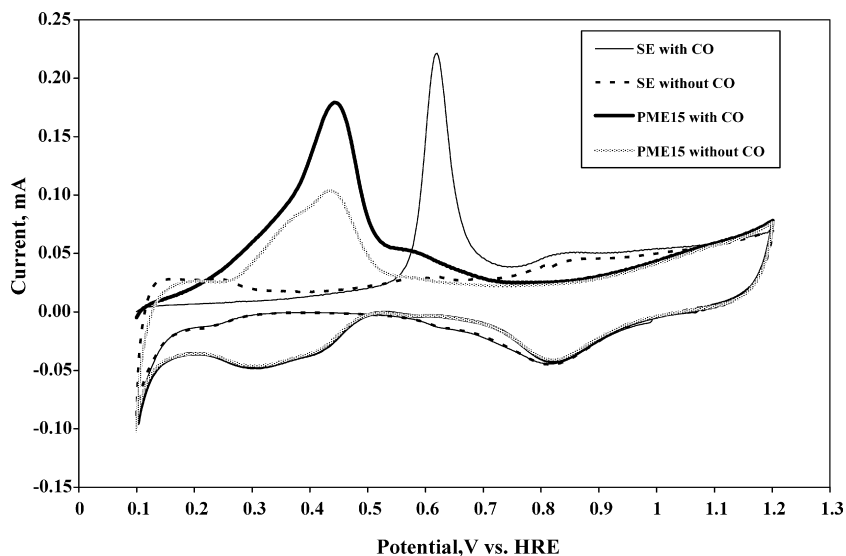
Fig. 5. Linear sweep CO stripping voltammograms for SE and PME15 electrodes at $T = 80\,^{\circ}C$.

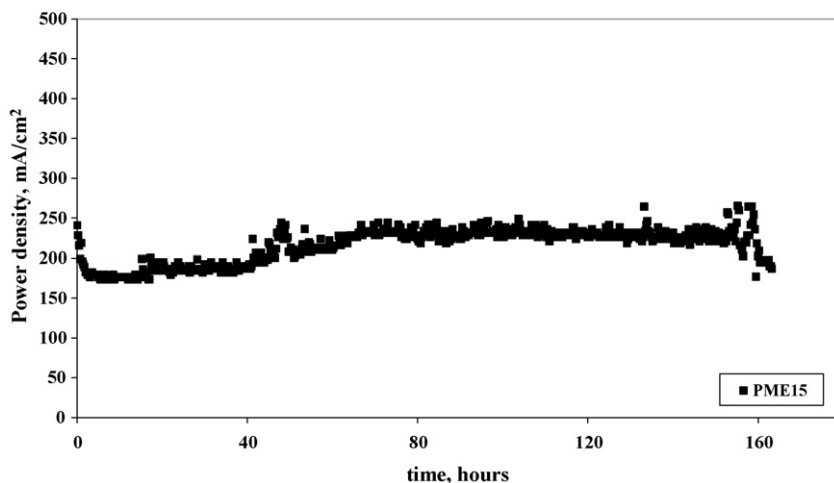Fig. 6. Short stability test of PME15 MEA in H_2–CO (100 ppm)/air at 80 $^{\circ}$C.

still present in the absence of CO. A second peak, partially overlapping the first, is present at about 0.58 V and it is due to the CO oxidation process onto the Pt sites. This peak is shifted compared to the SE, indicating an interaction between the Mo and Pt particles, to improve the CO tolerance. This means that it

is not necessary to have a direct contact between the two metals, as expected when the bifunctional mechanism occurs, since there is a further contribution due to a chemical heterogeneous reaction consuming CO, that is the water–gas shift reaction. The ECSA value, calculated for PME15, is 45 $m^2\,g^{-1}$, that is about
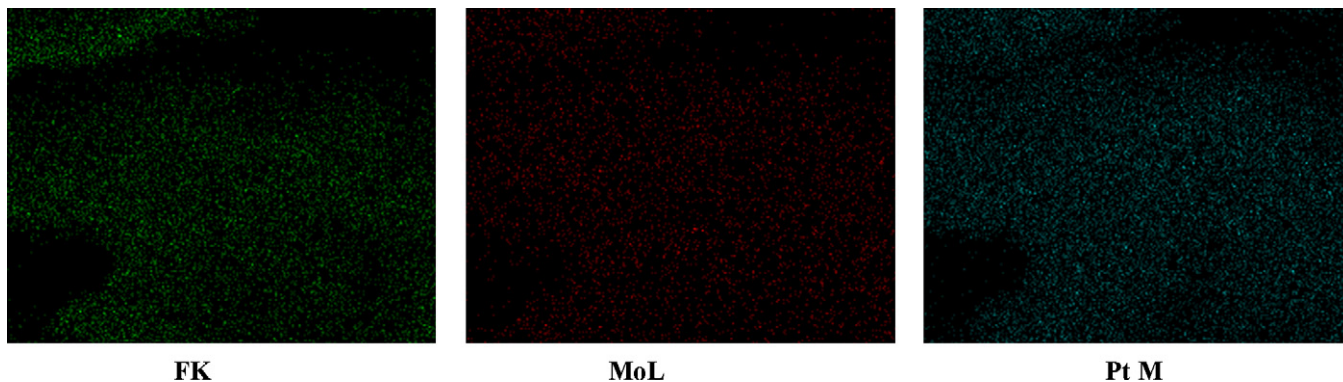

FK　　　　　　　　　**MoL**　　　　　　　　　**Pt M**

Fig. 7. F, Mo and Pt-mapping of PME15 electrode after the short stability test in H_2–CO (100 ppm)/air at 80 $^{\circ}$C.

one half of the value obtained for SE. The presence of PMoA in the catalytic layer provokes a reduction of the catalytic activity when the cell is fed by pure H_2 while, it promotes the catalytic activity through CO oxidation.

Moreover, to evaluate the promising results obtained during the previous tests, a short term stability test of about 160 h on PME15 MEA at $T = 80\,°C$ (100% RH) in H_2–CO (100 ppm)/air was carried out. Fig. 6 shows such a time-test in terms of power density.

An average power density of about $220\,mW\,cm^{-2}$ at a cell potential of 0.4–0.5 V was recorded.

To confirm the presence and, above all, to verify the dispersion homogeneity of the PMoA onto the PME15 electrode surface, a post-mortem EDX mapping was conducted after the time-test. Fig. 7 depicts the mapping of molybdenum (Mo), fluorine (F) and platinum (Pt). It is evident that Mo is present and homogenously dispersed onto the electrode surface compared to the two other elements (F and Pt) that constitute the catalytic layer, in particular, the Platinum of the electrocatalyst and fluorine of the Nafion® ionomer.

4. Conclusions

An evaluation of the influence of different amounts of PMoA in the catalytic layer was carried out, in terms of cell performance and CO poisoning. An improvement in the CO tolerance was obtained proportionally to the increase of the percentage of PMoA in the electrodes. A power density of about $240\,mW\,cm^{-2}$ at 0.6 V, independently on the used fuel, with a PMoA content of 15% (w/w) in the catalytic layer (PME15) was obtained. The CO stripping voltammograms indicates an interaction between the Mo and Pt particles, to improve the CO tolerance. The ECSA value, calculated for PME15, is $45\,m^2\,g^{-1}$, that is about one half of the value obtained for SE. The presence of PMoA in the catalytic layer provokes a reduction of the catalytic activity when the cell is fed by pure H_2 while, it promotes the catalytic activity through CO oxidation.

A short time-test was carried out for about 160 h at $80\,°C$ in H_2–CO/air with an average power density of $220\,mW\,cm^{-2}$ confirming the stability of the system.

The stability of PMoA in the catalytic layer after electrochemical tests was verified by EDX mapping. In addition, X-ray measurements were carried out on an impregnated carbon with PMoA in the same weight ratio used in the PME15 electrode, to simulate the absorption of the heteropolyacid on the electro-catalyst and to verify the presence of the inorganic compound onto the carbon after a solubility test. These measurements highlighted the presence of PMoA before and after the solubility test, confirming the stability of the heteropolyacid compound.

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