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ABSTRACTS

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ELECTROXIDATION OF H₂ ON Pt/C Pt-Ru/C AND Pt-Mo/C ANODES
FOR POLYMER ELECTROLYTE FUEL CELL

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1. Introduction

In the PEFCs the anode gas stream is H₂ rich, produced by reforming or partial oxidation of hydrocarbons and containing CO. The most efficient catalyst for the electrochemical oxidation of hydrogen (HOR) is constituted by Pt nano-particles supported on carbon (Pt/C). However such a catalyst is subjected to poisoning by the CO present, even at very low concentration (10 ppm). A possible solution for this problem consists in the use of CO tolerant electrocatalysts formed by alloying Pt with a second transition metal (e.g., Ru, Mo). So far, the best CO tolerant electrocatalyst appear to be the Pt-Ru (1:1) alloy, which is four times more active than pure Pt in H₂+100 ppm CO anode gas. However such an alloyed catalyst is less active than Pt in pure H₂ anode gas, thus before studying the effect of the CO-poisoning on alloyed catalysts, it is necessary to fully characterize their behaviour in pure H₂. The interpretation of both the E vs. i plots and the current distribution in membrane electrode assemblies (MEAs) with Pt-M/C (M=Ru or Mo) anodes at different atomic ratio (fed with pure H₂) is quite complicated. At low current densities the cathode kinetic limitation is predominant and hides the anode contribution. At high current densities, the ohmic resistance and the cathode mass transport limitations predominates the overall cell behaviour. It is only by means of half-cell measurements that it is possible to evaluate the behaviour of Pt-M/C anodes. In this paper we show that such electrodes are characterised by kinetic limitation, which influence the overall cell performance.

2. Experimental

Commercially available Pt/C, Pt/Ru/C (1/1 atomic ratio) and Pt-Mo/C (3/1, 4/1, 5/1 atomic ratio) catalyst powders on carbon black (Vulcan XC72) were obtained from E-TEK Inc. All materials had the same total metal loading (30 wt%). Three-layer (substrate/diffusive layer/catalyst layer) gas diffusion electrodes were prepared using a spray technique described in detail in previous works [1]. In all electrodes the Pt loading was kept constant at 0.50 mg cm⁻². A Pt/C with Pt loading of 0.11 mg cm⁻² was also prepared. The MEAs were made by hot pressing the electrodes on the Nafion 115 membrane. All anodes were used in combination with 20 wt% Pt/C cathodes (Pt loading of 0.5 mg cm⁻²). Electrochemical measurements were carried out by using a half-cell set-up at 25°C and a full-cell set-up at 80°C elsewhere described [1,2]. Electrochemical impedance spectroscopy (EIS) measurements on half cell were carried out in H₂, in the frequency range 20 kHz-0.05 Hz at open circuit potential (OCP). Galvanostatic polarisation (E vs. i) was carried out in the same cell configuration as for EIS measurements. The full-cell E vs. i measurements were carried out with a 50 cm² cell incorporated in test facility. Measurements were carried out at 80°C in H₂/Air (3/3 bar absolute pressure) with the humidification temperature of 90°C for H₂ and 85°C for air. The overall ohmic resistance was measured by current pulse transient technique from 0.0 to 0.3 A cm⁻².

3. Results and discussion

The anode galvanostatic polarisation data (in half-cell) in pure H₂ at 25°C in 1 M H₂SO₄ are shown in fig. 1. All the experimental data are fitted, using a Levenberg-Marquardt algorithm, with the following semi-empirical non-linear equation;

$$E = E_{\text{ocp}} + R_{\Omega} i + R_{\text{p}}^{\circ} i \exp(f i) \quad (1)$$

where the term E_{ocp} represents the anode open circuit potential (OCP), R_{Ω} the ohmic resistance, R_{p} the polarisation resistance at OCP and “ f ” a mass transport related factor. As the current density approach zero, the exponential term goes to the unity and all the electrodes show the typical linear behaviour. The eq.1 can be written as:

$$E = E_{ocp} + (R_{\Omega} + R_p^o) i \quad (2)$$

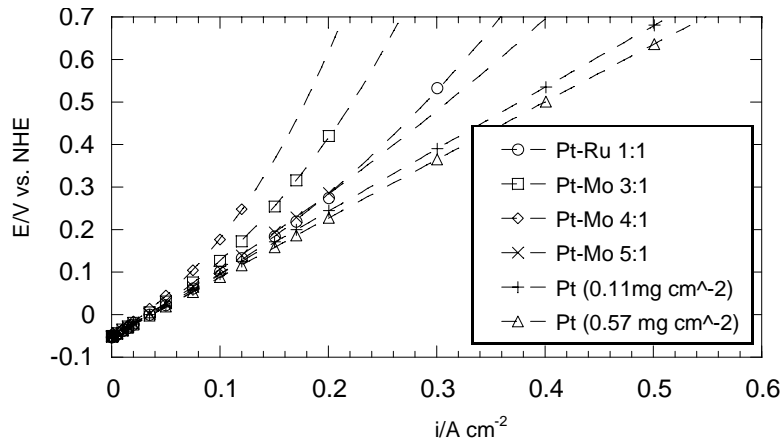


Fig. 1 - Galvanostatic steady-state polarisation curves, in half-cell, for gas diffusion electrodes in 1 M H₂SO₄ at 25°C, under H₂ flux. Dashed lines are based on fitting obtained with eq. 1.

At high current density only Pt/C electrodes maintain a linear trend independently from the Pt loading while all the Pt-M/C electrodes show a deviation from linearity. The ohmic and polarisation resistance (R_{Ω} , R_p^o) for each electrode were obtained by means of EIS. In tab.1 are summarised up the parameters obtained for each electrode by EIS data and fitting procedures. The R_p^o shows the trend; (Pt/C) \ll (Pt/Ru=1) \leq (Pt/Mo). The R_p^o at OCP and the anode performance appear to be strictly related. It is evident that the mass transport related factor “ f ” is inversely proportional to the limiting current density (i_{lim}). The expression of the i_{lim} for the HOR on catalysed gas diffusion electrodes, is given by the equation:

$$i_{lim} = nFC^o \sqrt{\%_{wt} A \rho (1 - \pi) \cdot D \cdot k_{at}} \quad (3)$$

where n represents the number of electrons, F the Faraday constant, C^o and D respectively the solubility and the diffusion constant of the hydrogen in Nafion, k_{at} the anodic Tafel chemical rate constant, π and ρ are respectively the porosity and the density of the carbon support, $\%_{wt}$ is the active catalyst metal loading (30%_{wt}), A is the total metal surface.. A decrease of the i_{lim} can be ascribed to a decrease of A or k_{at} , being all other terms constant. Using eq. 3 for Pt/C and Pt-M/C we obtain the relation:

$$i_{lim}(Pt/C) / i_{lim}(Pt-M/C) = \sqrt{A \cdot k_{at}} / \sqrt{A' \cdot k'_{at}} \quad (4)$$

where A , k_{at} and A' , k'_{at} represents respectively the active surface and the constant rate for Pt/C and Pt-M/C electrocatalysts. The active surface, obtained by means of XRD measurements, was 60 m²/g for Pt-Mo/C, 120 m²/g for Pt-Ru/C and 90 m²/g for Pt/C. An estimation of the limiting current density of Pt/Mo and Pt/Ru made by substituting the XRD area values in eq. 4, and considering equal k and k' , show that the different values of the active surface cannot explain the experimental decrease of the calculated i_{lim} for Pt-M/C (tab.1). However, a simultaneous decrease of constant rate k'_{at} in eq. 4 for Pt-Mo/C and much more for Pt-Ru/C can justify the reduction of i_{lim} . The decrease of k'_{at} for HOR on these kind of electrodes appear confirmed by the observed correlation between the kinetic parameters R_p^o and the mass transport related factor f . We used in our previous work [3,4], the Heyrowsky-Volmer mechanism to explain the lower rate constant of the HOR on Pt-Ru/C and Pt-Mo/C alloys. Analysing the imaginary part of impedance vs. the frequency for each electrode, the maximum of impedance appears at two different ranges of

frequency, which can be inversely related with two processes, characterised by different RC time constant [5]. In Pt-M/C anodes HOR proceeds by a process characterised by a RC time constant 200÷500 lower than Pt/C electrode. The increase of RC time constant is influenced by the Ru or Mo presence and involves oxygenated species (H_2O , OH^-) adsorbed on second metal sites.

Electrode	E^0/mV	$R_{\Omega}/ohm\ cm^{2*}$	$R_p^o/ohm\ cm^{2*}$	$f/A^{-1}cm^{-2}$	$i_{lim}/A\ cm^2$
Pt-Ru 1:1	-54±2	1.37	0.164	2.2±0.1	0.56
Pt-Mo 3:1	-50±2	1.34	0.188	8.4±0.1	0.25
Pt-Mo 4:1	-53±2	1.54	0.266	11.0±0.3	0.17
Pt-Mo 5:1	-53±2	1.42	0.167	2.4±0.1	0.53
Pt	-52±2	1.38	0.018	-	>0.8

Table 1 - Kinetic and mass-transport parameters obtained by EIS data* and by fitting of E vs i data with eq. 1 for Pt/C, Pt-Ru/C and Pt-Mo/C anodes.

Fig. 2 shows the cell performance of MEAs with Pt/C and Pt-Mo/C anodes at 80°C in H_2/air . MEAs with Pt-Mo/C anodes showed lower performance than Pt/C one. Inside the Pt-Mo catalysts, the performance order is: (Pt/Mo=3)>(Pt/Mo=4)>(Pt/Mo=5).

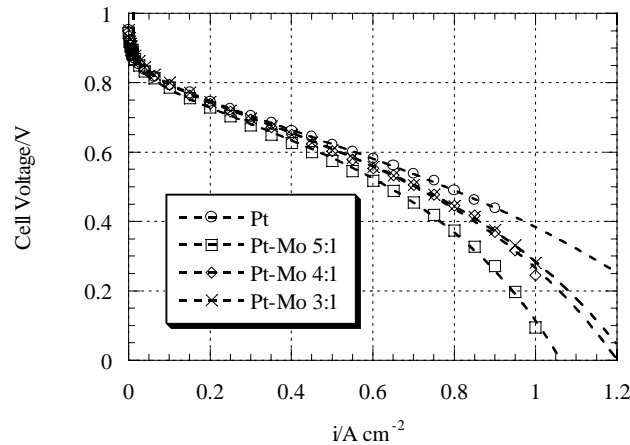


Fig. 2 – E_{cell} vs. i for Pt/C and Pt-Mo/C, $T_{cell}=80^\circ C$, H_2/air flux at 3/3 bar. Dashed lines are based on fitting obtained with eq.5.

The experimental E vs i data for MEAs were fitted using the semi-empirical eq.5 proposed by Ticianelli et al. [5]. The latter resistance (R_i) is the sum of: ohmic resistance (R_{Ω}), the polarisation resistance for the HOR (R_p), and the mass-transport resistance in the intermediate current density region (R_m). Difference of anode performance can then be attributed to a change of the R_p for the HOR, considering constant all other terms. Table 2 shows the parameters obtained by fitting experimental cell data E vs. i with eq. 5 and the R_{Ω} measured by means of current interrupt technique.

Electrode	$b/mV\ dec^{-1}$	E_0/mV	$R_i/ohm\ cm^2$	$R_{\Omega}/ohm\ cm^{2*}$
Pt	-55±1	775±3	0.34±0.01	0.20
Pt-Mo 5:1	-52±2	781±3	0.44±0.01	0.16
Pt-Mo 4:1	-53±2	785±4	0.40±0.01	0.20
Pt-Mo 3:1	-52±2	790±3	0.40±0.01	0.22

Table 2 - Kinetic and mass-transport parameters obtained by means of current interrupt technique and fitting of polarisation data with eq. 5 for Pt/C and Pt-Mo/C anodes.

The difference between R_i and R_{Ω} for Pt/C (0.14 ohm) can be considered from the contribution of the cathode mass transports resistance R_m in the linear current density region, neglecting the very

low R_p for HOR. The internal resistance R_i of the MEAs with Pt-Mo/C anodes is about 60-100 mohm cm^2 higher compared to the Pt/C ones. Such a high R_i can be attributed completely to the growth of the anode R_p . The evaluation of the best atomic ratio of MEAs with different Pt-Mo/C anodes by full-cell measurements is very difficult because the changes of anode contribution to R_p are only about 10% of the overall resistance R_i . Uncontrolled variations of the R_m and R_Ω can seriously affect the E vs i data. However at high current, the cell voltage decreases much more rapidly than expected according to eq. 5, particularly with Pt-Mo/C anodes, so a new equation was proposed to account for the departure from linearity of the E vs. i plots:

$$E = E_0 + b \log i - R_i i \quad (5) \quad E = E_0 + b \log(i) - i R_\Omega - i R_p^\circ \exp(f i) \quad (6)$$

The eq. 6 describes the E vs. i plot over the entire current density range, as illustrated in Fig. 2. The terms R_p° and f are related respectively to the anode polarisation resistance and to the cathode and anode mass transfer phenomena. The parameter R_p° associated to the anode polarisation resistance was always found in the range 70-100 mohm cm^2 . The differences between anodes are restricted in a limited range of 30 mohm cm^2 . Unpredictable effects can easily hide these low anode differences. The MEAs with Pt-Mo/C 5:1 anode show an anomalous behaviour with a high $R_p^\circ f$ value suggesting the presence of a mass transport problem not only related to anode limitation. Nevertheless, also the half-cell measurements show that the behaviour of Pt-Mo/C anodes at different atomic ratio is not easily explained. The kinetic of Pt-Mo alloys for HOR in acidic media appear to be influenced mainly by the unstable Mo oxidative states/forms and much less by the Pt/Mo atomic ratio [6]. In every case, the results in half-cell configuration show that anodes with very low Pt/Mo ratio, can reach same performance of Pt/Ru=1. This can be explained considering that molybdenum can be present as Mo^{+III} , Mo^{+IV} and Mo^{+VI} in our operative conditions and it can co-ordinate more H_2O molecules than ruthenium. Taking in to account the hypothesised Heyrowsky-Volmer mechanism for HOR on Pt-M electrodes [3,4], less atoms of Mo are needed to obtain the same adsorbed water than ruthenium.

4. Conclusions

The paper shows that a new empirical equation (eq.1) fits well the E vs. i data of Pt/C, Pt-Ru/C and Pt-Mo/C gas diffusion anodes. The physico-chemical interpretation of all parameters used in the equation is given. The observed i_{lim} decrease of Pt-M/C can be related partially with the change of the HOR rate constant. The Heyrowsky-Volmer mechanism for the HOR in Pt-Mo/C and Pt-Ru/C was proposed. The anode polarisation resistance of Pt-M/C electrodes in the PEFCs operative conditions was shown to affect the cell performance. A new equation (eq.6) was proposed to take into account for the departure from linearity of E vs. i data. Some Pt-Mo anodes showed performance comparable to Pt-Ru (1:1) anode. However, further studies on Pt-Mo alloys with respect to the oxidation states and chemical composition of Mo are needed to ascertain their stability in the PEFC operative conditions.

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