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## HYDROGEN OXIDATION REACTION ON BINARY ELECTROCATALYSTS FOR PEFCs

A. Pozio, L. Giorgi, C. Bracchini, E. Antolini

ENEA, C.R. Casaccia, Via Anguillarese 301, 00060 S. Maria di Galeria, Italy

Polymer Electrolyte Fuel Cells, PEFCs, could provide in a near future a primary power source for terrestrial electrical vehicles fed with reformed hydrogen-rich gas. A problem with this fuel is the presence of CO, which even at ppm levels, drastically affects cell performances, poisoning the electroactive sites of Pt/C anode. To solve this problem a typical approach is to use electrocatalysts more tolerant to CO than pure Pt/C, such as Pt-Ru/C and Pt-Mo/C alloys.

We report here comparative studies of the hydrogen oxidation reaction (HOR) of Pt/C, Pt-Ru/C and Pt-Mo/C electrodes. It was studied the effect of Ru and Mo content in the catalytic layer anodes with regard to hydrogen and carbon monoxide oxidation. Electrochemical impedance spectroscopy (EIS) and galvanostatic polarisation were used to characterise the electrochemical behaviour of the gas diffusion anodes in a half-cell configuration with H<sub>2</sub>SO<sub>4</sub> 1M at 25°C as the electrolyte. With regard to hydrogen oxidation, the catalytic performances were Pt/C > Pt-Ru/C ≥ Pt-Mo/C.

The addition of 100 ppm of CO to the hydrogen gas stream, decreased the catalytic performance of Pt-Ru/C and Pt-Mo/C about 10÷20 times and 700 times that of Pt/C (catalytic performances Pt-Ru/C ≥ Pt-Mo/C >> Pt/C).

Pt-Metal alloys showed same trend in performances in presence or in absence of CO, so indicating the existence of a different mechanism in the HOR respect to Pt/C electrode. EIS measurements on all Pt-Metal catalysts showed the presence and the influence of oxygenated species. In particular it seems to be a determining factor the oxidation state and/or hydration of the second metal (Ru or Mo), both on HOR and carbon monoxide oxidation.

The examination and non-linear regression of EIS spectra for Pt/C catalyst, showed the presence of a reactive process at high frequencies. At low frequencies the presence of diffusion and/or adsorption phenomena was evidenced.

The alloying of Ru and Mo to Pt decreases the hydrogen oxidation rate, by changing the mechanism, due to the presence of adsorbed intermediate species ( $\text{H}_2\text{O}$ ,  $\text{OH}^\cdot$ ). It exist an optimal Pt/Ru ratio (1/1), which minimises the impedance associated to the intermediates. The optimal Pt/Mo is 5/1, with performances comparable to Pt/Ru=1/1.

The behaviour of the alloys in presence of 100 ppm CO, has the same trend as in pure  $\text{H}_2$ . Therefore, we can suppose that: a) the presence of Ru or Mo has a positive effect regarding the CO tolerance; b) the  $\text{H}_2$  oxidation reaction is still enhanced by the ratios Pt/Ru=1 and Pt/Mo=5. For the Pt-Ru catalyst the two opposite effects (increase of  $[\text{H}_2\text{O}]_{\text{ads}}$  and reduction of Pt sites) still act. The HOR for the Pt-Mo catalyst is influenced by the oxidation state of Mo in presence of CO. The good tolerance of Pt-Ru alloys suggests the existence of a intrinsic mechanism not involving CO oxidation. Probably, on the Pt-Mo catalyst a double mechanism (intrinsic and promotion) is acting, because also at equilibrium potential the formation of oxides/hydroxides is possible.

An our hypothesis, to explain in which way the Pt chemisorption properties can change in presence of a ipo-electronic metal (Ru, Mo), is based on the electron donation/back-donation mechanism which acts in the Pt-CO bond. The CO adsorption on Pt is stabilized by two simultaneous effects: electron transfer (donation) from the CO filled  $5\sigma$  molecular orbital to the empty  $d\sigma$  band of Pt; back-donation of electrons from metal  $d\pi$  orbital to empty  $2\pi^*$  anti-bonding orbital of CO. The effect of the generation of a  $\sigma$  type bond strengthens the p type bond and vice versa.

In the Pt-Me alloys a modification of the empty electron states density happens, with a shift of the Fermi energy level respect to the energy of CO molecular orbitals. In such a situation the synergic mechanism of interaction of Pt-CO bond loses its stabilizing effect. Ipo-electronic metals, like Ru an Mo, produce a shift effect and charge redistribution, which strongly influences the CO adsorption phenomena.