

(1) e (2)



Electrochemical Division
Italian Chemical Society



GEI-98
Luigi Galvani
Anniversary Meeting

23-26 September 1998
Bologna, Italy



The Luigi Galvani Bicentenary
(1737-1798)

Pt, Ru AND Pt-Ru CATALYSTS DISPERSED ON CARBON: STRUCTURAL AND CATALYTIC CHARACTERISATION

C. Bracchini^a, L. Giorgi^b, A. Pozio^b, R. Giorgi^c, V. Indovina^a,
S. Turtù^c, E. Passalacqua^d

^aCNR-SACSO, Chemistry Dep., "La Sapienza" University, Rome, Italy

^bENEA, ERG-TEA-ECHI, ^cENEA, INN-NUMA-TECMA, Rome, Italy

^dInstitute CNR-TAE, Messina, Italy

To investigate the problem of Pt/C poisoning by CO in PEFCs (Polymer Electrolyte Fuel Cells) anode and to assess the role played by Ru, we studied commercial Pt/C, Ru/C and Pt-Ru/C powders (Ru/Pt=1/3 to 3 atomic ratio; metal loading 20 wt%). By XPS experiments, some spectroscopic features related to physical and chemical characteristics of these samples, were determined. Firstly, the energetic shift of the Pt 4f_{7/2} line in the powders with respect to reference platinum was studied to point out the electronic structure evolution from bulk to clusters, and, in case, a charge transfer indicative of alloy formation. Variations of the FWHM of Pt 4f_{7/2} was noticed, possibly due to either metal-metal and catalyst-support electronic interactions, Pt oxidation or oxygen adsorption, as well as to cluster size effect. In this frame, the Pt 4f doublet was decomposed by a curve fitting routine to evaluate the relative amount of the different valence states. Ru enrichment with respect to the nominal composition, underlined by XPS, contrary to bulk analysis (see EDS results), is discussed. Ru 3d_{5/2} main peak was not taken into account, due to the strong overlap with the high C 1s signal; a secondary transition, say Ru 3p, was considered only for quantitative purpose. A mean size of the metal particle of about 2 nm was determined for all the catalysts by X-Ray diffraction from the analysis of Pt(111) or Pt(220) line broadening. In the XRD spectra of Pt-Ru/C only the diffraction peaks of Pt were present and the angular position of these peaks shifted positively as Ru was increased, suggesting respectively Pt-Ru alloying and the progressive decrease of the cell parameter, a_{fcc} , with Ru. A decrease in the average size passing from Pt/C (2.6 nm) and Ru/C (2.8 nm) to the alloys (Pt-Ru 3:1, 1.9 nm, Pt-Ru 1:1, 2.1 nm and Pt-Ru 1:3, 2.1 nm) was determined by TEM. The bulk compositions of Pt-Ru/C, experimentally evaluated by SEM/EDS microanalysis, well matched the nominal compositions. The catalytic activity for CO oxidation by O₂ was investigated both in dry and wet atmosphere. In the temperature range 300 to 350 K, the turnover frequency (CO molecules s⁻¹ surface Pt and Ru atoms⁻¹) on Pt-Ru/C progressively and markedly increased with Ru content. The Pt/C catalyst was 20-200 times less active than Pt-Ru/C (depending on Ru content) and 90 times less active than Ru/C. The addition of water vapor to the reactant stream left the catalytic activity of Ru/C unchanged and that of Pt/C almost unchanged but at low temperatures it markedly improved that of Pt-Ru/C. These findings suggest that fuel cells equipped with Pt-Ru/C anodes perform better than cells with Pt/C anodes because the presence of surface oxide species on Ru promotes the oxidative removal of a CO molecule adsorbed on a next Pt site by providing the oxygen atom required for CO oxidation to CO₂.