

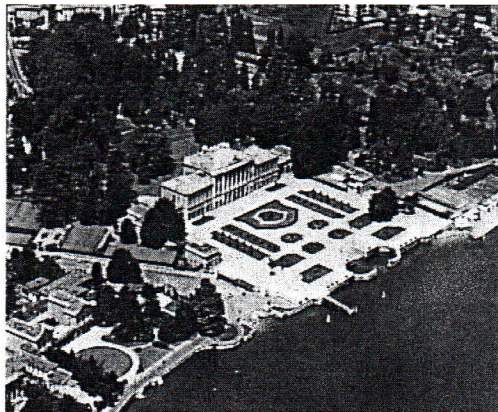
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RELATION AMONG ELECTRONIC STRUCTURE, PARTICLE SIZE DISTRIBUTION AND ELECTROCHEMICAL ACTIVITY OF Pt-BASED NANOSIZED ELECTROCATALYSTS

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The catalytic activity of nanosized metal particles dispersed on high-surface supports is known to be influenced by their size and electronic structure, which in turn determine the surface reactivity. In this work platinum based electrocatalysts Pt/C for PEFC have been considered. Gas-diffusion electrodes with a three-layer structure (substrate/diffusion layer/catalyst layer) were prepared, by using a combined spreading/spraying procedure [1]. The Pt loading was 0.1 mg cm^{-2} .

Electronic state of platinum clusters have been studied by XPS. The comparison of Pt 4f peaks between platinum bulk and platinum clusters of the Pt/C electrocatalyst evidenced that peaks from reduced size structures shifted towards high binding energy. Similar trend was observed in the complete electrodes, virgin(a) and thermal treated (b), as evidenced in figure 1. The peak FWHM also increased. Pt clusters of polarised samples (c,d) showed a tendency to Pt bulk features (c) [2].

Samples were analysed by XRD in order to obtain particle size distribution. Data were collected at glancing angle, focusing on the Pt (220) line. Distribution curves for Pt/C, virgin electrode and polarised sample reported in figure 2 were obtained by fitting the experimental data with a procedure described elsewhere [3]. The shape of the distribution, peaked on the small-particle side and with a tail on the large-particle side evidenced that particle growth is predominantly by coalescence. Moreover going from the Pt/C electrocatalyst to the polarised electrode, both the minimum size and the medium dimension of the particles increased.

The ageing tests were carried out by applying a galvanostatic polarization in cathodic conditions (0.1 A cm^{-2}). The electrode/electrolyte interface was investigated by electrochemical impedance spectroscopy (EIS), by collecting the data at different time intervals during the galvanostatic polarization. The comparison of E_c vs. i plots, before and after 56 hours of polarization, are shown in fig.3, together with the EIS data. The loss of performance can be attributed to the increase of catalyst particle size as confirmed also by the increase of polarization resistance.

It has been then established that the polarization induced surface migration of the clusters ad their coalescence, giving rise to the small variations observed in photoemission peaks, changes in the particles size distribution and the consequent decrease of the electrochemical active surface.

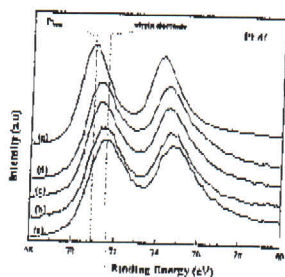


Figure 1

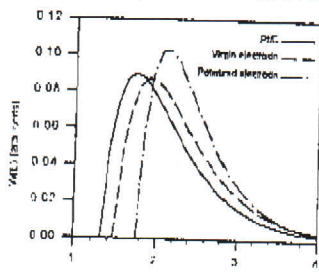


Figure 2

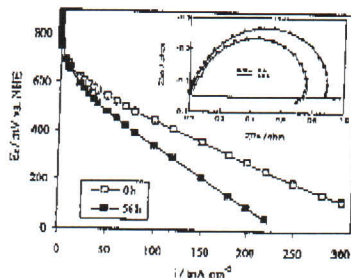


Figure 3

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2. R. Giorgi, P. Ascarelli, S. Turtù, V. Contini, *Applied Surface Science* 178 (2001) 149
3. P. Ascarelli, V. Contini, R. Giorgi, *J. Appl. Phys.* 91 (2002) 4556