

NEW MATERIALS FOR ELECTROCHEMICAL SYSTEMS IV

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Procedure for Comparing High Surface Pt/C Catalysts

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1. INTRODUCTION

The direct evaluation of various catalysts for their activity in the gas diffusion electrodes (GDEs) of PEFCs is time-consuming and expensive: hence it would be useful to devise a simple half-cell technique, which could mimic the complete fuel cell. Cyclic voltammetry (CV) has been frequently used to estimate the surface area of Pt/C catalysts by adsorption of atomic hydrogen in acidic media. Nevertheless the results obtained by different authors on a commercial Pt/C in the same or in different operative conditions are very discordant, also if they used the same catalysts (E-TEK). The preparative method of the gas diffusion electrode appears to be important. Three methods appear to be utilized in the preparative of catalytic layer of GDE: PTFE incorporated [1], Nafion impregnated [2], Nafion incorporated [3,4]. The cyclic voltammetry appears to be a good technique to obtain information on electrochemical active surface (EAS), but attention must be dedicated to establish a well-defined procedure. In particular the GDE preparative method appear to be fundamental.

2. EXPERIMENTAL

Carbon black (Vulcan XC-72) with a BET specific surface area of $250 \text{ m}^2 \text{ g}^{-1}$ was used as a support for all catalysts. Three different 20 wt% Pt/C catalysts were prepared using a proprietary method based on formiate reduction. Commercial available 20 wt% Pt/C catalyst powder (E-TEK) was used as a reference material. The cyclic voltammetry were carried out in a conventional airtight three-electrode cell containing 1M H_2SO_4 electrolytes at 25°C. The working electrode was adapted to a rotating disk electrode system. The active layers on the GDEs were prepared using a proprietary method briefly explained here. The experimental procedure was as follows: the three-electrode cell was purged with Ar for 15 min, subsequently, five consecutive cyclic voltammeteries (sweep rate 10 mV s^{-1}) were performed in the potential range 0-1400 mV vs. NHE. Pure CO was bubbled into the electrolyte for 15 sec and then its adsorption on the electrode was driven under potential control at 200 mV vs. NHE for one minute. The electrolyte was purged for 25 minutes with argon, keeping electrode potential at OCP vs. NHE to eliminate CO reversibly adsorbed on the surface. Three cyclic voltammeteries were recorded from 0 to 1400 mV vs. NHE. The first anodic sweep from 0 to 1400 mV vs. NHE was performed (sweep rate 10 mV s^{-1}) to electro-oxidize the irreversibly adsorbed CO and the subsequently voltammeteries in order to verify the completeness of the CO oxidation. X-ray diffractograms were recorded using a diffractometer (Cu K_α source), operated in the step scan mode with a 0.05 step and in the range of 15 to 90 (2θ).

3. RESULTS AND DISCUSSION

The average particle sizes and surfaces areas of catalyst were estimated from the strongest XRD Pt (111) peak (Table I). From CV data, the coulombic charges for hydrogen desorption (Q_H) were used to calculate the active platinum area after correction for double layer charge. The ratio $Q_H/[\text{Pt}]$ decrease as the platinum loading increase. These results clearly demonstrate that a wide range of EAS is obtainable simply by changing the platinum loading. The observed trend for EAS depends by the fact that in our calculation all platinum loaded on the electrode is considered electrochemically active. This assumption can be considered exact only in a well-established range of platinum loading. In fact as the platinum loading increase the thickness of electrode, as a consequence some platinum particles are blocked in the carbon substrate and not exposed to the electrolyte solution. On the

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other side, a too small amount of catalyst powder does not cover uniformly the electrode geometric area, so the EAS appear to be oversized. Besides the EAS mean error is a function of the inverse square of platinum loading, for this reason a too small platinum loading should be avoid. Fig.1 shows that an exact control of platinum loading it is necessary to compare different catalysts; values comparable with XRD data can be obtained using platinum loading in the range 0.40-0.67 mg cm^{-2} . Fig. 2 summarizes data obtained with three different techniques. The trend appear to be the same for all techniques, only the ENEA DF2 catalyst shows a higher EAS value respect to XRD data. The presence of a high fraction of not XRD detectable platinum particles on this sample (diffusion scattering and/or amorphous platinum) can justify this difference.

References

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Catalyst	H ₂ adsorption $\text{m}^2 \text{g}^{-1}$	CO stripping $\text{m}^2 \text{g}^{-1}$	XRD $\text{m}^2 \text{g}^{-1}$
ETEK	106 ± 17	97 ± 23	108 ± 16
ENEA DF4	100 ± 9	92 ± 13	93 ± 14
ENEA DF3	90 ± 12	79 ± 13	81 ± 12
ENEA DF2	60 ± 5	66 ± 15	49 ± 7

Table 1: Electrode surface area obtained by means of different techniques

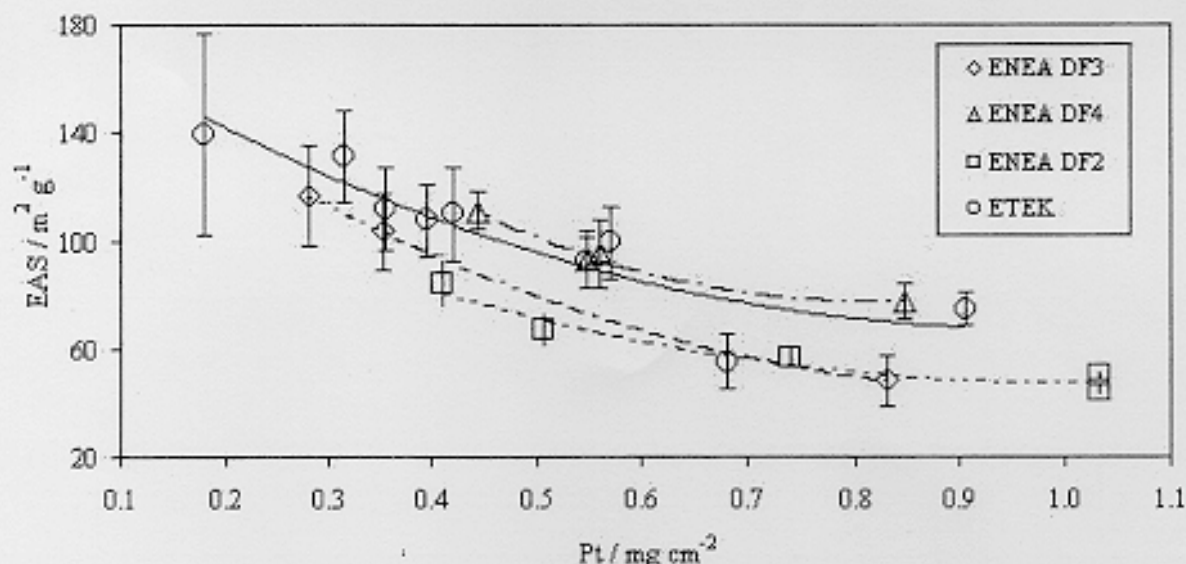


Figure 1: Calculated electrochemical active surface (EAS) vs. platinum loading for E-TEK and ENEA catalysts.

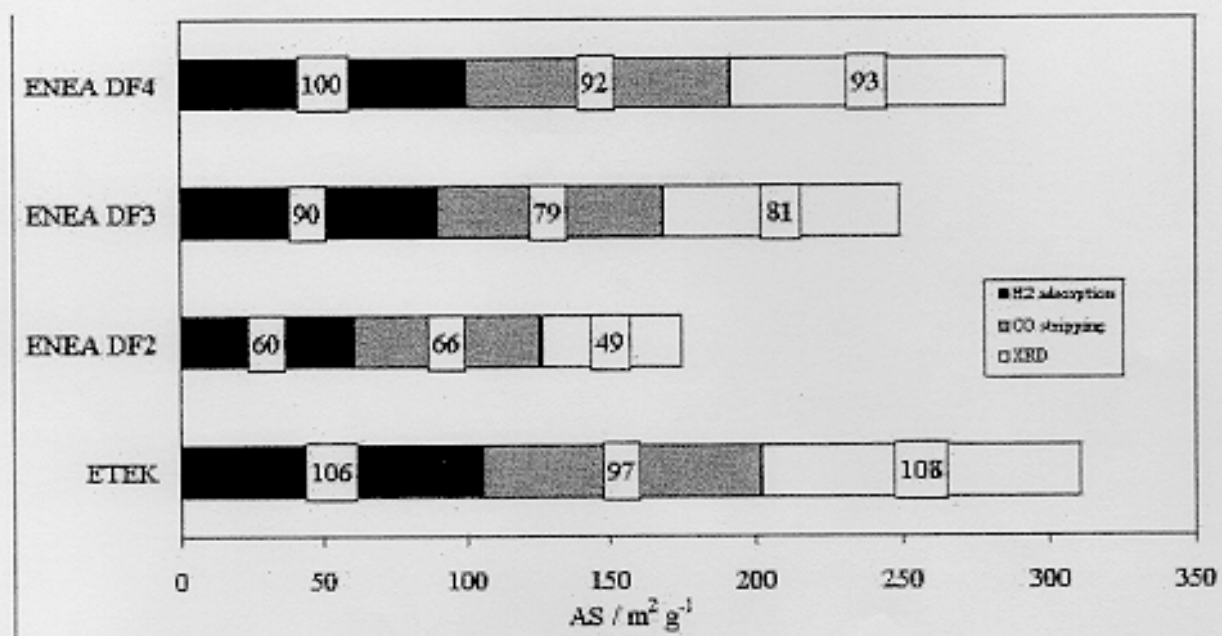


Figure 2: Comparison between active surface (AS) obtained with different techniques.