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Development of Low Platinum Catalytic Layers for PEM Fuel Cells

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Polymer Electrolyte Membrane Fuel Cells (PEMFC) are considered as promising energy sources for vehicle, portable and stationary applications. However, their commercial use is still limited due to the high cost and insufficient durability. The catalytic layers of the state-of-the-art PEMFCs are multi-component media comprising a carbon-supported Pt or Pt alloy catalyst, accelerating the rates of electrochemical reactions; an ionomer, providing flow of protons through the membrane-electrode-assembly (MEA); and gas- and liquid-filled pores, providing access of the reagents to and the products from the catalyst surface. In this presentation we discuss three different approaches to reduce the platinum metal loadings in a PEMFC. The first approach is related to the optimization of the support material; the second approach deals with the optimization of the catalytic layer architecture, while the third approach is based on the development of non-platinum catalysts for the anode of a PEMFC.

Carbon support materials strongly influence the (i) size and morphology of metal nanoparticles, (ii) catalyst stability, (iii) metal/ionomer contact and catalyst utilization, (iv) mass-transport and (v) water management, and hence are among the key factors affecting the FC performance. The role of carbon materials in the catalytic layers of the PEMFCs has been recently reviewed by Maillard *et al.* [1].

In order to unveil the influence of the carbon support porosity on the fuel cell performance, a set of Pt catalysts supported on carbons of the Sibunit family were prepared. The carbon supports varied in degree of activation and consequently BET surface areas ranging from 22 to 415 m²g⁻¹. The conventional 20 wt. % Pt catalyst supported on Vulcan XC-72 carbon black was used as a reference [2]. Fuel cell tests revealed strong influence of the type of carbon support both on the total and on the Pt mass-normalized currents. The highest mass specific currents are achieved for 30 wt. % Pt/Sibunit 20P and 40 wt. % Pt/Sibunit 619P with BET surface areas of carbon supports of 292 and 415 m²g⁻¹, correspondingly. Both of these exceed the activity of 20 wt. % Pt/Vulcan XC-72 catalyst, the enhancement factor varying from 4 to 6 depending on whether pure oxygen or air is fed to the cathode. The increased mass specific activities cannot be ascribed to the influence of the carbon support on the metal dispersion which was purposely kept constant and equal to *ca.* 0.3. Analysis of the I-U curves revealed that the improved cell performance is related to the improved mass transport in the cathode layers. The mass transport overvoltages were found to be strongly dependent on the specific surface area and on the texture of the support. This work proves that utilization of novel carbon materials, such as proprietary carbon materials of the Sibunit family, may lead to major improvements in the PEMFC performance, thus allowing to decrease considerably the amount of Pt in the catalytic layers.

We now move to the discussion of the novel catalytic layer architectures for the fuel cell applications. We propose three dimensionally ordered catalytic layers of aligned carbon nano-filaments as the means improve the mass transport, water management and electronic conductivity in the catalytic layer and, ultimately, the effectiveness of the Pt utilization [3]. The arrays of aligned carbon nano-filaments (ACNF) were synthesized by catalytic chemical vapour deposition on TiO_x substrates, obtained via oxidative treatment of either polycrystalline Ti or thin Ti films on Si(100). Figure 1 shows a SEM image of the ACNF. The Pt deposition on the ACNF was utilized to prepare a set of model catalysts, which were investigated in two fuel cell related processes: the oxygen reduction (ORR) and the hydrogen oxidation (HOR) reactions. At this stage the experiments were performed in a conventional three-electrode electrochemical cell in 0.1 M H_2SO_4 electrolyte. The experimental data were compared with the results of mathematical modelling performed for a fast (quasi)reversible and a slow irreversible electrochemical reaction.

For the HOR, high Faradaic current and high effectiveness of the Pt utilization can be obtained for the catalytic layers with high Pt coverage but low Pt loading. The results indicate that for a fast (quasi)reversible electrochemical reaction, such as the HOR, the best performance is provided by an ultra-thin quasi two-dimensional catalytic layer. For the ORR, although the Faradaic current increases with the Pt loading, the effectiveness factor is decreasing with the Pt loading and the thickness of the layer, already for fairly low Pt loadings.

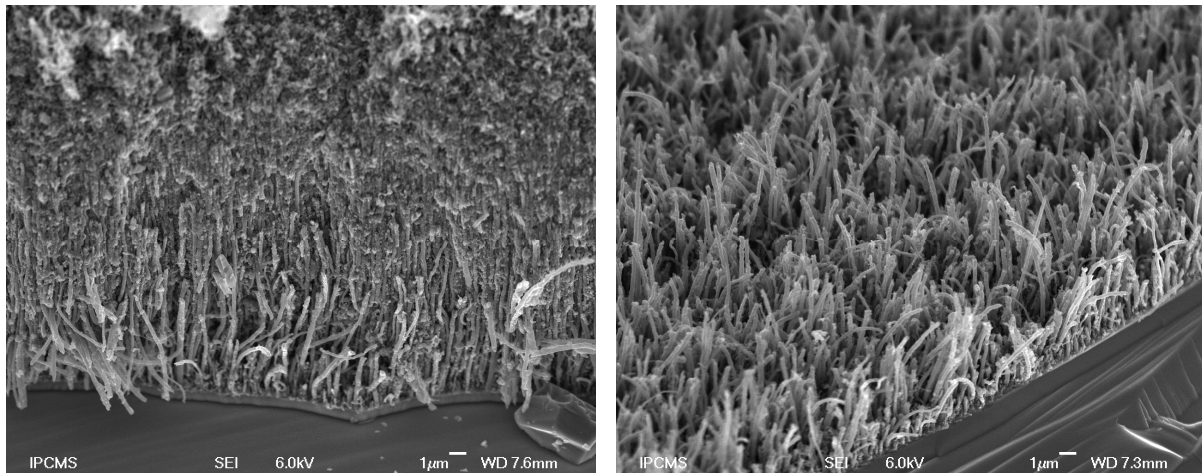


Figure 1: SEM images of ACNF grown on $TiO_x/Ti/Si(100)$ base: an integral ACNF layer (left-hand side), and the bottom part of the ACNF (right-hand side).

The influence of the Thiele modulus (TM) computed as $TM = L \sqrt{\frac{\Gamma_{Pt} k_{ORR}}{D_{O_2} R_{pore}}}$ on the specific activity in the ORR was analyzed. Here L is the height of the layer of ACNF, $R_{pore} = 100$ nm is the pore radius (estimated as half of the distance between the nearest fiber walls), D_{O_2} is the diffusion coefficient of O_2 in the aqueous electrolyte, and k_{ORR} is the electrode potential-dependent kinetic constant.

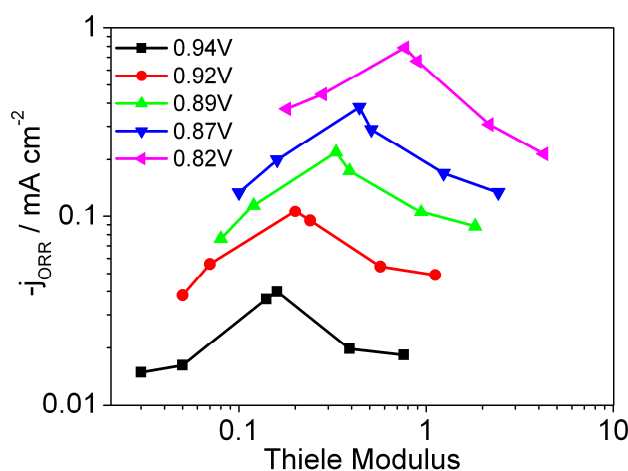


Figure 2: ORR current density extracted from the RDE curves measured in O₂-saturated 0.1 M H₂SO₄ at 30 °C, 5 mV s⁻¹ and 1600 rpm at different electrode potentials vs. Thiele modulus. Currents are normalized to the electrochemically active surface area of Pt.

The analysis of the specific activity in the ORR as a function of the Thiele modulus (Figure 2) suggests that the observed decrease of the effectiveness factor at high Thiele moduli is due to the diffusion hindrance in the pores. The drop of the specific activity at low Thiele moduli indicates that ultra-thin catalytic layers may not be advantageous for the ORR. This is attributed to the escape of the H₂O₂ intermediate from the catalytic layer and to the decrease of the effective number of transferred electrons from 4 to 2. Comparison of the specific activities of Pt nanoparticles within Pt/ACNF ($d_{Pt} = 4.1$ nm) with those of Pt/Vulcan XC-72 ($d_{Pt} = 3.7$ nm) shows that Pt/ACNF electrodes exhibit factor of 5 higher specific activity at an optimum Pt loading and layer thickness. This observation gives hope that structured catalytic layers may be useful for the future development of highly efficient, low noble metal loading catalytic layers for the PEMFCs. Further studies aimed at the incorporation of Pt/ACNF in the MEA and their utilization in the PEMFCs are in progress. The results will be reported elsewhere.

Finally, we consider the development of non-platinum Pd-Au/C [4] catalysts for the anode of a PEMFC fed with reformat. Palladium-gold particles with varied composition were prepared by Pd electrochemical deposition on Au nanoparticles immobilized on a model carbon support. While the hydrogen oxidation activity of Pd/C [5] and Pd-Au/C [4] catalysts is inferior to that of Pt/C, their CO-tolerance is much superior.

It was found that the decrease of the effective Pd overlayer thickness below ca. two monolayers resulted in a two-fold increase of the exchange current density of the hydrogen oxidation reaction and in a significant increase of the CO tolerance (Figure 3). Testing Pd-Au/C catalysts in PEMFCs is now in progress and will be reported elsewhere.

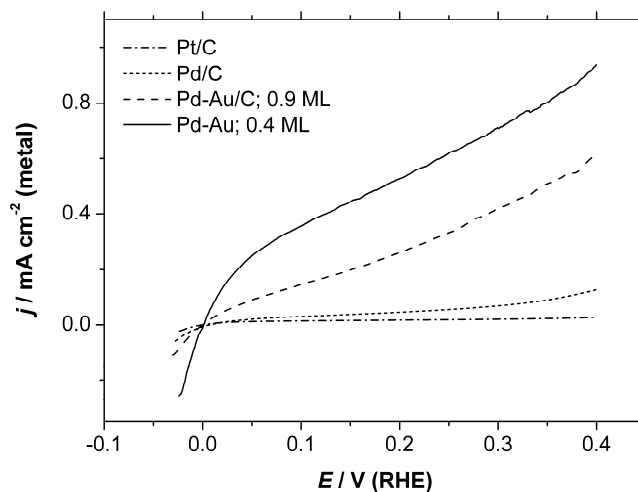


Figure 3: Hydrogen electrooxidation curves on CO-blocked Pd-Au/C surfaces in H₂-saturated 0.1 M H₂SO₄ at 60 °C and 2500 rpm. Currents are normalized to the total metal surface area. The coverage of Au particles with Pd is given in monolayers (ML).

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