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The Influence of Catalyst Layer Thickness on the Performance and Degradation of PEM Fuel Cell Cathodes with Constant Catalyst Loading

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ABSTRACT

Three catalytic layers containing Pt nanoparticles supported on high surface area carbon of different Pt loading but with the same total amount of platinum and therefore of different thickness were employed as cathode catalytic layers (CCLs) in a PEM fuel cell. The layers were subjected to a degradation protocol with an upper potential limit of 1.5 V. Upon exposure to the degradation protocol particle size increased, the electrochemical areas (ECAs) of the catalysts decreased, the catalytic layers became thinner, and the average pore size decreased, indicating both carbon and Pt corrosion. The relative decrease in the ECA was approximately the same for all three layers and was therefore approximately independent of CCL thickness. For all samples the reaction order with respect to oxygen was one half and the samples showed doubling of the slope of the potential vs. log current curve ($dE/d\log i$) at high current densities. This indicates that kinetics control the potential at low currents and kinetics and proton migration (ohmic drops in the catalytic layer) at high. However, the degradation protocol also introduced limitations due to oxygen diffusion in the agglomerates. This led to a quadrupling of the $dE/d\log i$-slope in 13% oxygen in the samples with the highest catalyst area per volume. For the sample with the lowest catalyst area per volume this slope increased by a factor of six in 13% oxygen, indicating that the local current density exceeded that required for the Tafel slope of the oxygen-reduction reaction (ORR) to double.

1. Introduction

To overcome the cost issue as a major barrier limiting the large-scale commercialization of proton exchange membrane fuel cells (PEMFCs) is a central focus of PEMFC research [1–6]. An important part of the PEMFC for which substantial cost reductions would be possible is the catalytic layer, which typically consists of carbon material, ionomer and platinum. In a typical PEMFC catalytic layer a Pt electrocatalyst is supported on a carbon black such as Vulcan XC-72 which has a low cost and high availability. Given the limited availability and high cost of precious metals such as Pt, optimization of catalyst layer structure is of particular importance for large-scale PEMFC deployment. Evidence exists to show that catalyst layer imperfections such as a spot with restricted metal loading have a substantial effect on both membrane-electrode assembly (MEA) performance and durability [7–9]. This shows the importance of studies on catalyst layers in the larger context of PEMFC commercialization.

The thickness of the catalyst layers have been shown experimentally [10–15] and theoretically [16–23] to be decisive in determining the performance of the layers. From the data of Wilson and Gottesfeld [24] a thickness of around 4μm appears to strike an optimum compromise in terms of catalyst utilization and performance for catalyst-coated membrane (CCM) electrodes. Ticianelli and co-workers [10] showed that performance of porous gas diffusion electrodes prepared by impregnating carbon cloth with Pt/C catalysts improved with increasing wt % of Pt in the Pt/C catalyst for a constant total Pt loading of 0.4 mg cm^{-2} and for catalysts of narrow and reasonably similar size distributions. However, these electrodes were impregnated with Nafion® for which the penetration depth into the carbon-cloth support were the same in all cases. Paganini et al. [13] performed similar studies on

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electrodes prepared by applying catalyst inks to the diffusion layer electrodes by brushing for a number of catalytic layers differing in thickness but with a constant total mass of Pt per geometric area ($0.4\,mg\,cm^{-2}$). Also in this case did the performance improve with increasing wt % of Pt in the Pt/C catalyst and thus with decreasing thickness of the catalytic layer.

In addition to affecting the effectiveness and overall performance of the catalytic layers the electrochemical characteristics may also change. da Silva and Ticianelli [12] showed that the slopes of the potential vs. log current density curves (i. e. $dE/d\log i$ where E is the potential and i the current density) are very sensitive to the thickness of the catalytic layers, c. f. also Ref. [16]. Characterization of carbon-cloth supported Pt/C electrodes in aqueous solutions of H_2SO_4 demonstrated an increase of the $dE/d\log i$ slope from approximately 70 mV at low current density up to almost four times this value at high current densities. A comparison with theoretical models led to an interpretation according to which various limiting factors kick in at different potentials, including an inherent change in the Tafel slope of the oxygen-reduction reaction (ORR), diffusion limitations in flooded agglomerates containing the catalyst, and ohmic losses in the CCL. Processes at the PEMFC cathode are thus very complex, and complicated transport and electrochemical reaction phenomena are operative in the porous cathode catalytic layer (CCL) simultaneously.

An issue as important as the performance *per se* is the durability of the CCL. Thermodynamically the carbon support is expected to oxidize to CO_2 and CO at potentials higher than 0.2 V vs. the reversible hydrogen electrode (RHE) [25]. On the other hand, under fuel cell operating conditions and cathode potentials around 0.6-0.9 V vs. RHE, the kinetics of carbon corrosion are still quite slow. In practice, potentials higher than 1.2 V vs. NHE are required to corrode the carbon support at sufficiently high reaction rates to cause a significant degradation to the PEMFC electrode [26].

Recent research [27] indicates that the CCL experiences a significant thinning upon being exposed to degradation protocols. It appears however, that few studies exist that investigate the dependence of the stability of PEM-cathodes on initial CCL thickness. It is well known that the potential is not evenly distributed in porous electrodes [28], and therefore there may be a thickness dependence also for CCL stability since stability is related to the (local) potential in the electrode. Degradation also depends on the chemical environment and thus on transport rates, which may differ in a thick electrode from those of a thin. Thus, due to either low proton mobility in the CCL, in the presence of oxygen transport limitations, or both, the electrochemical reaction will occur unevenly in the catalytic layer. Therefore a decrease in the catalyst layer thickness (by design or as a consequence of corrosion) would not necessarily affect the electrochemical performance proportionally. In consequence the effect of current and potential distributions in thick and thin catalyst layers is important in terms of CCL degradation and for which deeper studies are needed. An understanding of such effects will also form an important basis for efforts towards understanding the role of catalyst layer variations [29].

The scope of this work is thus to investigate role of the catalyst layer thickness with respect to degradation and corrosion and MEA electrochemical performance, but with a constant total loading of the catalyst. The cathode was chosen for the study since the rate-determining chemical reaction and the lion's share of the activation overpotential losses take place in this region. Degradation in cathodes therefore merits attention for durability studies of PEMFCs. In this study a well-controlled synthesis technique was used to control the Pt-particle dispersion in the CCL and also to produce samples with almost the same range of particle size to limit the effect of the latter on performance and durability of the electrocatalysts [30,31]. The samples were subsequently subjected to accelerated degradation tests (ADTs) by subjecting the cathode to potential cycling between 0.6 V and 1.5 V. Our tests thus differ from those proposed by the U.S. Department of Energy (DOE) [32], for example, by exposing the electrode to a more extensive potential range. The DOE tests aim at simulating the gradual degradation of the entire catalyst in normal PEM fuel cell operation. Here, however, we aimed at simulating the effects of typical potential excursions suffered by the cell during start-up/shut-down conditions, under which conditions the cell may be exposed to potentials as high as 1.5 V [33]. We expect these conditions to promote carbon corrosion. The results below will demonstrate that the performance is independent of thickness for a given Pt loading and for typical thicknesses employed in PEM fuel cells. For degradation processes, on the other hand, we aim to show that thickness does matter in layers with a constant total Pt content.

2. Experimental

2.1. Catalyst synthesis

Materials and solvents were obtained from commercial suppliers and were used without further purification. Carbon black (Vulcan XC72, CABOT Corporation), hexachloroplatinate (IV) (Johnson Mattey, Pt content: 39.76 %, purity ≥ 99 %), sodium hydroxide (VMR, purity ≥ 99 %), ethylene glycol (Sigma-Aldrich purity ≥ 99 %) and analytical grade acetone were used to synthesize the catalyst by the adsorption polyol (AP) method explained in detail elsewhere [34,35]. Briefly, 1.0 g of H_2PtCl_6 was dissolved in 250 ml of ethylene glycol followed by addition of 100 ml of $0.5\,mol\,dm^{-3}$ NaOH in ethylene glycol to maintain the pH slightly basic. The mixture was then heated at 145 °C for four hours under nitrogen flow. The carbon support was suspended in ethanol by ultra-sonication for 15 minutes, after which the metal colloidal solution was added to the solution. The pH of the mixture was adjusted to around 2 by addition of $1\,mol\,dm^{-3}$ HCl followed by sonication for another 10 minutes. The mixture was then stirred at 55 °C for 18 hours during which N_2 was bubbled through the suspension. The solution was cooled down and centrifuged. The catalyst was then washed repeatedly with acetone and finally water, and dried at 70 °C for 500 minutes. The same batch of Pt colloidal solution was used for all the metal loadings, viz. for 10% (PtC10), 20% (PtC20) and 30% (PtC30).

2.2. TEM analysis

Transmission electron microscopy (with a JEOL JEM-2010) was performed on the samples to estimate the particle size and study the metal distribution on the support as well as the morphology. TEM was also used to check for presence of aggregates or isolated platinum nanoparticles in the catalysts.

We estimated particle size from the high resolution TEM images, and assuming spherical particles we employed the following equation for the overall surface area, $S_{overall}$,

$$S_{overall} = \frac{6 \times 10^3}{\rho \times d} \quad (1)$$

where $\rho = 21.4\,g\,cm^{-3}$ is the density of Pt and d is the particle size [36].

2.3. Thermal gravimetric analysis

Thermal Gravimetric Analysis (TGA) was conducted on a NETZCH, STA449C thermogravimetric analyzer using a flow of air in the temperature range 25 through 800 °C to determine the actual Pt loadings on the carbon supports.