Tailored porosities of the cathode layer for improved polymer electrolyte fuel cell performance

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HIGHLIGHTS

- A new technique, that introduces micrometer sized pores in the nanoporous catalyst layer, is tested.
- The technique uses monodisperse polystyrene particles as pore formers.
- Macropores in the nanoporous layer improves the polymer electrolyte fuel cell performance.
- Results are obtained for catalyst loading which are twice the US DOE target for 2020.

GRAPHICAL ABSTRACT
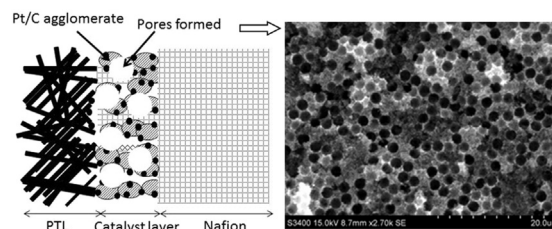
ABSTRACT

We show experimentally for the first time that the introduction of macro-pores in the nanoporous catalyst layer of a polymer electrolyte membrane fuel cell can improve its performance. We have achieved a Pt utilization of about 0.23 mg W^{-1} at 0.6 V which is twice the value of the DOE target for 2020, and three times (0.60 mg W^{-1}) smaller than the value of a fully nanoporous reference layer at a catalyst loading of 0.11 mg cm^{-2}. In this work, monodispersed polystyrene particles with diameters of 0.5 and 1 μm were used as pore formers. Cathode catalyst layers with macroporous volume fractions between 0 and 0.58 were investigated. Maximum performance was observed for fuel cells with a macroporous volume fraction of about 0.52 for a 1 μm thick catalyst layer. The results, which were obtained for the cathode layer, support earlier theoretical predictions that gas access to and water escape from the catalyst can be facilitated by introduction of macropores in the nanoporous layer.

1. Introduction

The use of the polymer electrolyte membrane fuel cell (PEMFC) for transport applications requires electrodes that produce a high power density with low catalyst loading. The US-DOE has set the target of reducing the PGM (Pt group metal) content to about 0.125 mg W^{-1} for automotive use in the year 2020 [1]. This implies that PEMFCs must be able to operate at high current densities with an acceptable reduction in cell potential and low material costs. High current densities mean significant ohmic losses in the membrane and high cathode overpotentials. Operations at high current densities lead to insufficient oxygen supply to the cathode. Water clogging of the pores can also hamper oxygen access. This will create oxygen concentration gradients across the catalyst layer resulting in decreased fuel cell performance.

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The first significantly improved PEMFC performance was achieved when the thin film MEA catalyst layer with low platinum loading (~0.1 mg cm^{-2}) was introduced in 1992 [2,3]. Since then, different methods that improve the performance and reduce the Pt utilization further, have been reported [4—26]. Attention has been given to modifications of pore structure, e.g. by using different catalyst supported carbons [4,5], to variations in the carbon composition [6], to varying Nafion content [7—10] and to pore formers of various sorts [11—15]. The importance of the morphological properties of the gas/water supply pathway on the performance has been studied extensively; see e.g. Refs. [16—19]. The morphology of the catalyst layer, however, has only recently been addressed [20—26]. The relation between the pore size, morphology, distribution and synthesis, and the cell performance is therefore not fully understood.

Kjelstrup et al. [20] proposed a systematic route to MEA design. Using the experience that minimum energy dissipation can be obtained with uniform driving forces [21,22], a strategy was proposed to minimize concentration polarization in the PEMFC. The strategy was inspired by theoretical work of Wang and Coppens [24] for effective heterogeneous catalysis. It was predicted that better performance with lower Pt utilization was achievable by the introduction of optimal macropores in the catalyst layer [20]. This would facilitate a more uniform and rapid distribution of oxygen and product water than in a fully nanoporous layer. There is not yet such general procedure adopted in the production of MEAs, and the present work, along with our recent publication [14], can be seen as first steps in this direction. We have chosen to investigate the effect on the cathode where the potential for improvements are largest.

In their theoretical optimization procedure, Kjelstrup et al. [20] found the optimal macroporosity and the height of the catalyst layer in the polymer electrolyte fuel cell. As a calculation example, they used the standard E-TEK Elat/Std/DS/V2 gas diffusion electrodes with 0.5 mg of Pt cm^{-2} catalyst loading, and 20% Pt/C on Vulcan XC-72 as a catalyst support. It was found that the amount of catalyst could possibly be reduced by a factor of 4—8, while the energy efficiency for the same conditions (high current density) could be increased by 10—20%. It was further shown that an optimal macroporosity existed when the pore volume fraction was 0.5. The optimum was shallow (see Fig. 3 in Ref. [20]), meaning that a variation in 0.5 by ±0.2 units did not make much of a difference for the outcome of the calculation. The upper bound of the pore diameter was 0.5 μm. The value obtained for the thickness of the catalyst layer (4 μm for a current density of 1.5 A cm^{-2}) depended on assumptions of (i) a first-order reaction at the cathode, (ii) the value of the gas diffusion constant for oxygen (iii) the oxygen concentration in the inlet flow.

It is not trivial to create catalyst layers which have a uniformly distributed macroporosity. To use indentation techniques, templates etc. is close at hand [11,12,14], but these procedures are costly and cumbersome at their present stage of development. We ourselves were struggling to fabricate catalyst layers with pores <2 μm through template-assisted indentation methods [14]). The theoretical results mentioned above are useful in this situation, as they make clear that the exact value of the macroporosity, as well as the pore shape is not essential for achieving improvements. To us, this means that it is not necessary to implement straight and well defined channel-like macropores into the nanoporous catalyst layer.

For this reason, we have turned our attention to the possibility offered by polystyrene monodisperse particles [14]. The fact that they are monodisperse means that we can determine the volume fraction of macropores that they can introduce in the catalyst layer. In this work, we have chosen to work with particles of diameter 1 and also 0.5 μm. We have not been able to go below the smallest

diameter yet, and a larger diameter will disturb the charge-conducting pathways too much. The values chosen can be seen as approximations to the optimal theoretical value of 0.5 μm [20]. We shall see that the fuel cell with 0.5 μm pores perform better than the one with larger pores.

The idea of the procedure is schematically pictured in Fig. 1. The figure shows the half-cell that contains the cathode before (a) and after (b) the introduction of macropores. The reference cell (a) has a fully nanoporous catalyst layer with Pt/C particles in contact with the Nafion 212 membrane on one side and a porous transport layer (PTL) or the current collector on the other side. Test cell (b) shows homogeneous macropores created by introduction of polystyrene particles in the nanoporous catalyst layer. The membrane and PTL are the same in Fig. 1b and a. In Fig. 1a, the reacting gas is supplied to the catalyst particles through nanopores only, while in Fig. 1b, the reacting gas can travel in two types of pores, one large with diameter 0.5 or 1.0 μm, and one small with a nanometer diameter. The large pores serve as a short-cut path for the gas to the catalyst, and a better escape possibility for water in the reverse direction. The total layer thickness in the Figure is 1 μm, meaning that there is space for maximum one sphere of diameter 1 μm, but two layers of particles having a diameter 0.5 μm. The last case is illustrated in Fig. 1b.

We show first how the monodisperse particles can be added to the synthesis mixture and removed before the MEA is made. The resulting layer, with macropores embedded in a nanoporous mixture, is tested under normal fuel cell conditions. We shall see that the results agree with the theoretical predictions [20]. Microspherical cavities with 0.5 μm diameter, packed to a volume fraction 0.52 in a layer of thickness 1 μm, improve the catalyst utilization (mg W^{-1}) by a factor of three compared to a reference layer without macropores. Although the performance of fuel cell with larger macropores is comparatively inferior it is still better than the reference cell without any macropores.

We explain in Section 2 how the novel catalyst layers with pore formers were made and tested for fuel cell performance. Scanning electron micrographs (SEM) were taken to ensure that we created a homogeneous porosity. The results from the first tests of the effect of monodisperse pore formers, described in Section 3.2, confirm the theoretical predictions made, which leads us to conclude in Section 4 that this line of research should be pursued.

2. Experimental

2.1. Preparation of membrane electrode assembly

The schematic preparation process of a paste for the catalyst layers was described in our previous publication [14]. A conventional anode was used, to be able to conclude on the cathode performance directly. Porous transport layers (PTLs) of type H2315 I2 C6 from Freudenberg (FCCT), to be used as anodes, were manually sprayed with 40 wt% Pt/C to give a loading of about 0.4 mg cm^{-2}. In the reference experiments we used this layer also at the cathode.

Monodispersed polystyrene particles were introduced as pore formers in the cathode catalyst layer only. The polystyrene particles with the diameters of 0.5 and 1.0 μm were synthesized in-house by the Division of Polymer and Composite Materials at SINTEF Materials and Chemistry. The amount of polystyrene particles to be tested was dispersed in water and added to the catalyst ink. The ink was prepared by mixing 60 wt% Pt/C (Alfa Aesar GmbH&CoKG) with isopropanol and deionized water (ratio 4:1) with 17 wt% Nafion solution (DuPont Inc.) with respect to Pt/C, and polystyrene particles with wt% 0, 30, 50, 70 or 90 with respect to Pt/C. The Pt loading in the dry cathode catalyst layer was fixed between 0.10 and 0.12 mg cm^{-2}. This serves as our reference catalyst for