How the colloid chemistry of precursor electrocatalyst dispersions is related to the polymer electrolyte membrane fuel cell performance

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HIGHLIGHTS

- PEMFC fuel cells were prepared from colloid-chemically modified electrocatalysts.
- Improved layer morphology leads to higher performance at high current density.
- Electrocatalyst activity is not affected by colloid-chemical tuning.

GRAPHICAL ABSTRACT
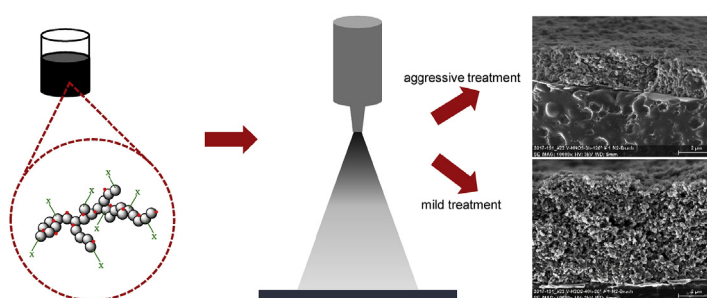
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ABSTRACT

Polymer electrolyte membrane fuel cells (PEMFCs) operating at low temperature (60–80 °C, up to 110 °C) are mostly limited in their performance by the kinetics of the oxygen reduction reaction (ORR), leading to high loadings of platinum (Pt) in the cathode. Pt catalysts are without alternative in numerous industrial applications, and since Pt resources are limited, the associated high costs for low temperature fuel cells are hindering among other factors their commercialization. In order to increase the fraction of electrocatalytically available Pt towards ORR, this work is devoted to the factors responsible for the microstructure of the PEMFC cathodes. Typically, the active layers are coated by processes like spraying, doctor blading, printing etc. Therefore, the final structure actually is strongly dependent on the coating process and the physicochemical properties of the catalyst dispersions used. Selecting commercially available electrocatalysts from *Johnson-Matthey* and *Tanaka* as active material and ultrasonically assisted spraying as the coating method, systematic variations of the surface chemistry of the catalyst particles and their influence on catalyst layer morphology and therefore electrical and electrochemical properties of resulting membrane electrode assemblies (MEA) have been investigated. It could be shown, that the colloid–chemical properties of the catalyst dispersions have a profound influence not only on the microstructure of the MEAs but also on the performance under operating conditions.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) using H_2 as fuel should be an ideal solution for automotive application [1]. They run at low temperatures (normally 60–80 °C), do not contain aggressive or toxic media and thus are inherently safe (disregarding potential H_2 –storage issues). However, at low-temperature conditions due to the sluggish oxygen reduction reaction (ORR, at the cathode) high loadings of noble metal electrocatalyst dominated by platinum (Pt) are required [2]. High cost and scarcity of Pt is an essential barrier to the widespread commercialization of PEMFCs, and therefore any measure that has the potential to reduce the necessary amount of Pt is highly welcome [3]. Apart from the search for new catalyst concepts without any metals [4,5] or work to optimize or modify existing catalyst systems based on noble and alloys with non-noble metals [6], optimization of the electrode morphology by tuning the colloidal properties of the catalyst precursor dispersion is an approach, that does not require new types of catalyst, nor new coating technologies, but has the potential to improve electrochemical catalyst utilization. Since only those Pt sites that are part of the three-phase boundary (electrons, protons and gaseous reagents) will be catalytically active, the microstructure of the active layer (cathode catalyst layer, CCL) in the membrane electrode assembly (MEA) is of major importance [7,8]. Increasing the over-all availability of Pt in the MEA will not only reduce the required Pt loading, but may also decrease the amount of ionomer employed, which also is an expensive component of an MEA. Of course, there are further requirements for the catalyst layer: electronic and ionic conductivities need to be as high as possible in order to avoid ohmic losses, and the pore system must be able to carry product water without flooding of the channel system and thus blocking the gaseous reagents access. These considerations make clear, that the MEA morphology is of uttermost importance for high performance PEMFCs and thus has attracted a number of both theoretical and practical studies [9–12].

For this study, MEAs are prepared using one of the standard, highly reproducible technologies available, namely ultrasonically assisted spraying of low-viscosity catalyst dispersions based on a water/alcohol/ionomer mixture. State-of-the-art catalysts are based on partially graphitized carbon particles of ca. 50 nm–300 nm particle size, decorated with Pt particles smaller than 10 nm [13–15]. For the spraying process, colloidally stable dispersions based on water, isopropanol and ionomer have to be prepared and then are sprayed in several layers until the desired material transfer has been reached. These dispersions need to provide sufficient colloid-chemical stability during the spraying process (avoiding agglomeration and precipitation), before the droplets formed hit the substrate, form a wet layer and undergo solidification. After spraying and drying at a substrate temperature of 150 °C the microstructure of the active layer is fixed and cannot be altered anymore, and any additives used (except very volatile components or water soluble materials) thus will remain permanently in the structure. Variations of the colloid–chemical state of the catalyst dispersions therefore are expected to directly influence the microstructure and thus the performance of the final MEA.

The approach applied in this study is focused on modifications of the carbon support surface chemistry [16,17], rather than changing the nature of the support radically, e.g. by employing continuous gel structures [18] or ordered scaffolds [19]. It is well established in the literature, that oxidative treatments of various kinds can introduce oxygen-containing functional groups on carbon surfaces [20,21]. These groups in turn are responsible for the colloid-chemical behaviour in dispersion: surface charges (characterized by their ζ-potential) and agglomeration tendencies due to hydrophobic interaction can be traced back to such functional entities. Oxidative treatment may be mild (using e.g. diluted H_2O_2 or $(NH4)_2S_2O_8$) or aggressive (using e.g. concentrated HNO_3 as explored for multiwalled carbon nanotubes [22–24]), introducing different kinds of surface groups and sometimes even carbon structure destruction and decomposition. Whether these

variants of oxidation have an influence on the active Pt particles and PEMFC performance, is still an open question. Treating supports and supported catalysts with oxidizing agents is not a new approach: it has been used to increase the adherence of the Pt-nanoparticles to the carbon support [17], to remove CO from the anode [14] or to increase the availability of PtRu in methanol electrooxidation [21]. For the present approach focused on the ORR cathode, pure supports as well as commercially available Pt and PtCo electrocatalysts supported on Vulcan XC72R (JM, TKK) are used and assessed in terms of colloid chemical parameters of the precursor dispersion, catalyst layer morphology and performance indicators for electrical and electrochemical behaviour in PEMFCs. The catalysts under test are: HISPEC4000 (40 wt %Pt/Vulcan XC72R) from *Johnson Matthey*, TEC10VA50E (46.2 wt%Pt/ Vulcan XC72R) and TEC36VA52 (46.8 wt%Pt + 6.6 wt%Co/Vulcan XC72R) from *Tanaka* (TKK). It is expected, that any chemical modification of this non-porous support will happen exclusively on its surface and thus affect directly the colloid chemical behaviour in dispersion and during film formation. Moreover, since primary particle size (30–50 nm) and general morphology (secondary hard aggregates of 200 nm–300 nm length and with variable width) of well-dispersed Vulcan XC72R are well documented and reproducible, any change of these parameters by the pre-treatments investigated can easily be followed.

The basic consideration behind this study is the following: particles in a well-stabilized dispersion (like the ink used for spraying) are protected by electrostatic charge or steric effects against agglomeration. During layer formation (incl. drying) however, this protection needs to break down, in order to allow ionomer–coated particles to get into contact close enough to establish attractive forces (e.g. of *van-der-Waals*–type). These contacts need to be homogeneously distributed, strong enough mechanically (since they define the final pore system) and close enough electrically (since they will be responsible for electron and proton conductivity of the support network). Weakly stabilized dispersion systems then are expected to lead to rather disordered layers of low density (particles stick immediately to neighbours during the fast drying process), whereas a strongly stabilized system will allow particles to settle in the layer during formation (as long as the protection against attraction is active during the drying process), eventually forming more ordered and dense deposits, at least when compared to the case of weak stabilization. These differences in layer morphology should have a profound influence on the performance of the MEA.

Spraying on a heated substrate will cause the solvents to quickly evaporate, or in other words, the concentration of carbon (electrocatalyst) particles will increase rapidly. From studies of pure (but unmodified) carbon particles in dispersion, it is well known, that a gel-like structure is being formed beyond a certain concentration, which can be assessed by rheometric or electrical measurements. These structures do form already in the fluid phase at effective volume fractions of around 0.2 for dispersions in propylene carbonate [25], in view of electrical as well as mechanical properties. The colloid chemistry of the liquid dispersion is becoming more and more concentrated in the drying process, therefore it is expected to have a significant influence on the pore structure, ionomer distribution and electrical contacts of the final deposit.

For PEMFC electrodes, neither very dense layers (hindering mass transport) nor very open layers (reducing the three phase boundary) are favourable. Therefore, it is expected, that a systematic variation of the stabilization strength will affect the cell performance and allow for finding an optimal point with respect to the resulting electrode morphology.

The experiments are split into two parts. First, a typical catalyst support (*Vulcan XC72R*) is treated by various oxidation procedures, dispersed into an ink and sprayed onto various substrates. The inks are tested for particle size and ζ–potential, and the resulting layers are then characterized with respect to their overall homogeneity, thickness, electrical conductivity and BET surface. Second, commercial carbon-