Pt based PEMFC catalysts from colloidal particle suspensions – a toolbox for model studies

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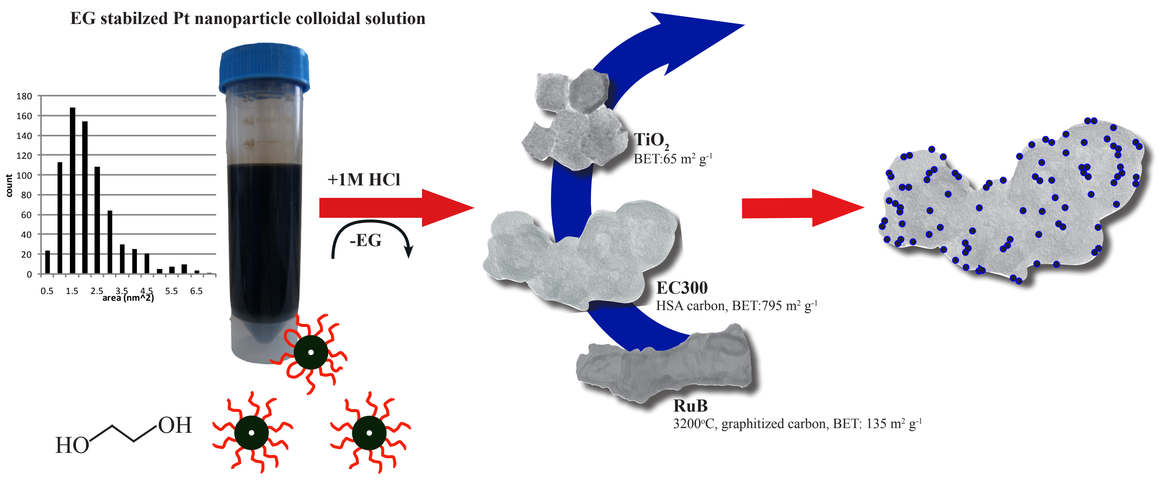
Abstract

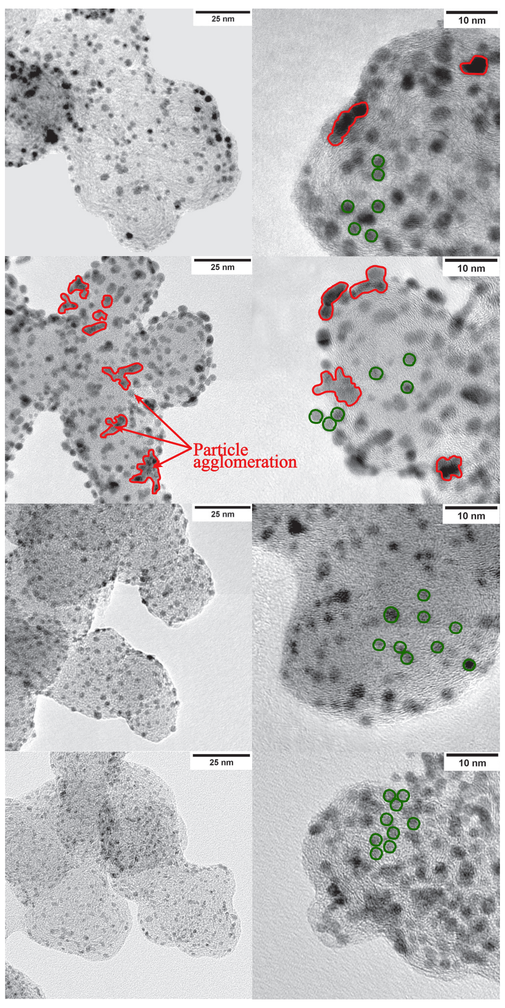
The objective of our work is to prepare and study catalysts that can help to understand and thereby improve the existing commercially available electrocatalysts. A typical PEMFC catalyst consists of high surface area carbon supported Pt or Pt-alloy nanoparticles. Previous studies report – sometimes with contradicting conclusions – on the influence of the support, particle size and composition on the ORR activity and the electrochemical stability. In general however, these studies do not selectively change only one of the variables, for example the Pt loading, while leaving the others constant, e.g. the particle size. In our work we introduce a reliable, artefact-free method for studying these effects by synthesising carbon supported, Pt based catalysts from colloidal dispersions of well defined Pt NPs synthesized by a ethylene glycol method [1].

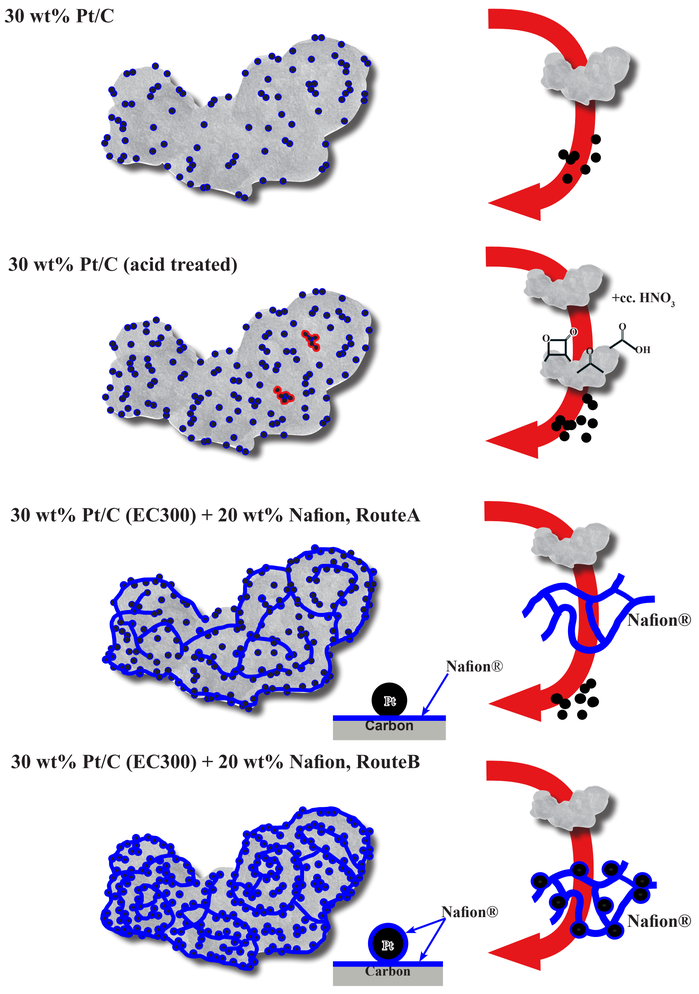
Preparation of model catalysts by EG colloidal method

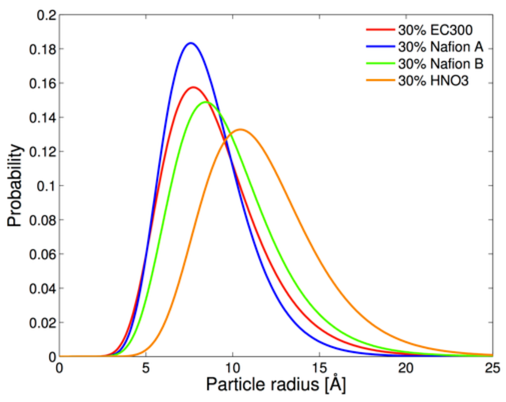


The ethylene glycol (EG) method allows us to produce small metal particles with a narrow size distribution. It is a very powerful method to produce catalysts, because it enables us a controlled synthesis of catalysts where individual parameters such as particle size, support material and Pt loading can be tuned without changing other parameters.

Physical characterization of model catalysts by TEM and SAXS





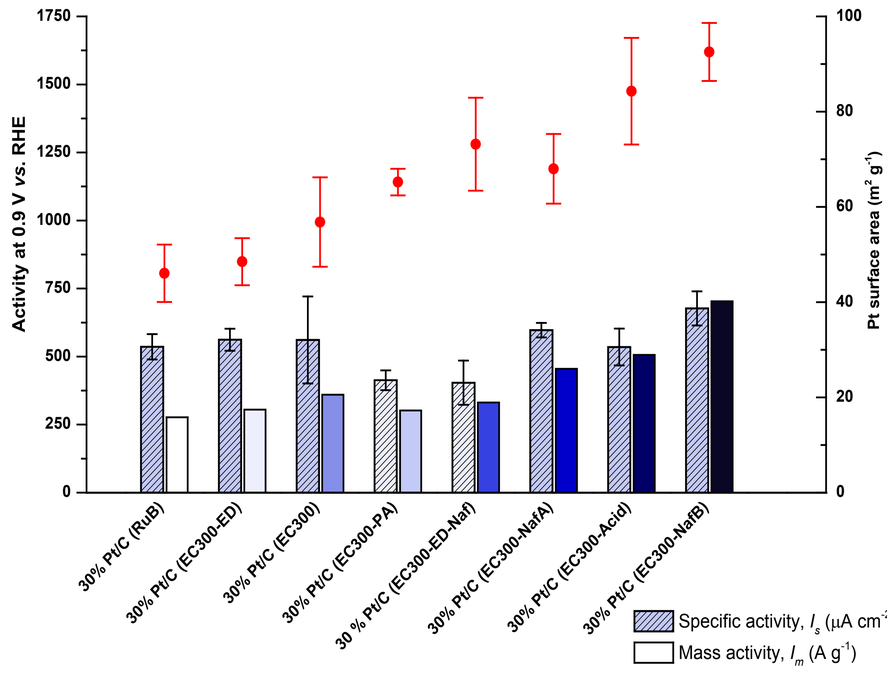


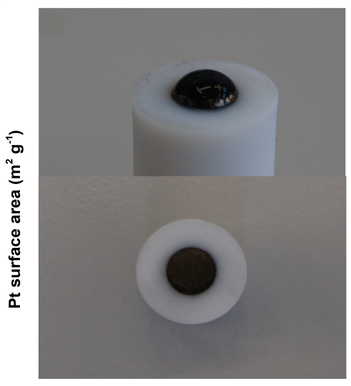
The combination of TEM and SAXS is beneficial as they are complementary methods for the evaluation of the structural properties of PEM fuel cell catalysts. The catalyst particle size and distribution of the catalysts were determined from SAXS data, while the particle dispersion on the carbon support were characterized by TEM. SAXS analysis yielded for the 30 wt% Pt/C (EC300) sample investigated here an average particle diameter of 1.5-1.6 nm with a fairly narrow distribution.

The TEM micrograph of the acid treated sample shows larger number of nanoparticle per surface area but also indicates a tendency for agglomeration. The majority of the particles present in the micrographs are larger - as compared with untreated sample - and the average size is 2.2 nm. Furthermore, it is seen that, the larger Pt particles consist of particles built up from single, smaller ones.

Nafion® incorporation has no impact on the particle size, but significantly enhances the metal particle attachment to the carbon surface. As shown in the TEM micrographs, it improves not only the Pt nanoparticle attachment but also the dispersion through its extensive network; therefore the particles remain separated and evenly distributed.

Electrochemical characterization





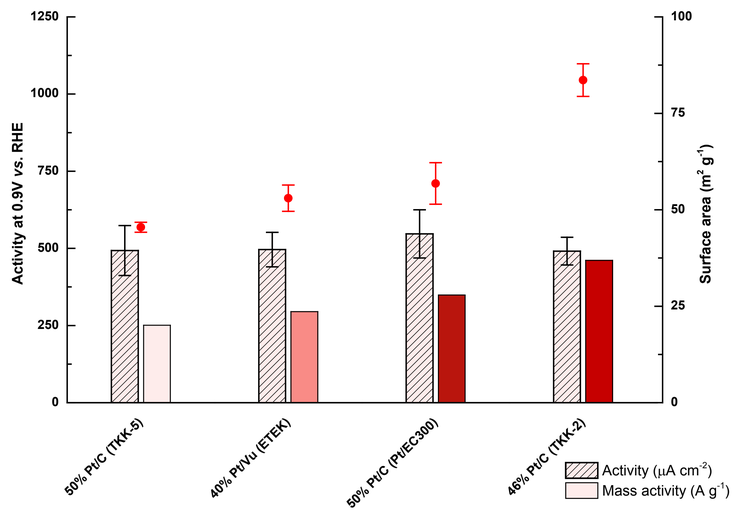
EC300	high surface area Ketjenblack
RuB	heat treated (3200°C) Ketjenblack
ED	N-doped carbon (ethylenediamine method)
PA	N-doped carbon (polyaniline method)
Acid	cc. 67.5 wt% HNO_3 treated carbon (8 hours)
Naf	Nafion® impregnation (20wt%)

Comparison of specific (I_s) and mass (I_m) activities of model catalysts for ORR in 0.1 M $HClO_4$, determined at 0.9 V *vs.* RHE

The electrocatalytic performance of the Pt model catalysts was characterized by the RDE thin film approach. The acid treatment and Nafion impregnation are found to be beneficial ways to enhance the electrocatalytic surface area. Most likely, acid treatment introduces a more hydrophilic surface structure and a larger number of oxygen-containing functional groups (-COOH, -OH, -C=O) that represents anchoring sites for Pt particle during the preparation process; however the catalysts nanoparticles are partly agglomerated. Nafion impregnation improves not only the Pt nanoparticle attachment but also the dispersion.

The carbon pre-treatment methods, such as N-doping and Nafion impregnation have no significant impact on ORR specific activity. Higher mass activity, >400 A g^{-1}_{Pt} is obtained for the catalysts with higher Pt surface area.

ORR activity vs. commercial catalysts



	Pt NP size (nm)	Carbon Support
TKK-5	~ 5	HSA carbon
ETEK	2.9	Vulcan XC-72
TKK-2	~ 2	HSA carbon
Pt/C	~ 2	EC300

TKK-5	Tanaka Kikinzoku Kyogyo
TKK-2	Tanaka Kikinzoku Kyogyo
ETEK	BASF

Comparison of specific (I_s) and mass (I_m) activities of commercial and model catalysts for ORR in 0.1 M $HClO_4$, determined at 0.9 V *vs.* RHE

Comparing the electrochemical properties of a series of commercial with our model catalyst, it is found that all specific activities of the investigated catalysts are around 500 µA cm^{-2}, while particle size and support of the investigated samples are different. Therefore, neither the catalyst particle size nor the carbon support material is found to be a key factor to influence the ORR activity in the investigated particle size window of 2-5 nm.

Conclusions

The ethylene glycol (EG) method is found to be effective way to disperse metal NPs on various carbon supports. The combination of our catalyst preparation method with the well-known characterization techniques (TEM, SAXS and RDE studies) allow us to identify the role of single parameters in the metal particle dispersion process and ORR activity.

For instance, one of the main findings of our study is the identification of a significant improvement due to Nafion® impregnation . More particles are attached to the support material - and are better dispersed by remaining separated on the carbon surface.

The advantage of our approach in comparison to study commercially available catalysts is the capability to identify single parameters that may have a crucial role in the improvement of PEM fuel cell electrocatalysts.

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[1] Tractable Platinum, Rhodium, and Ruthenium Nanoclusters with Small Particle Size in Organic Media, Chemistry of Materials, 12 (2000) 1622-1627.