

Black and green: catalyst and membranes for fuel cells

Relevant for: dynamic light scattering, electrophoretic light scattering, laser diffraction, streaming potential, PSA, Litesizer, SurPASS 3

The global energy landscape is changing rapidly and the demand for smart, environmentally friendly and cost effective energy solutions is growing. Fuel cells represent the green alternative to the battery world. They stand out due to their high efficiencies of up to 60 % and reach increasing importance in stationary applications but also in the transportation sector. In this application report we will discuss the role of particle size, zeta potential and surface zeta potential in the development and quality control of catalyst and ion exchange membranes for fuel cells.



1 Introduction

A fuel cell is an electrochemical cell that converts the chemical energy of a fuel such as hydrogen, and an oxidizing agent, such as oxygen, into electricity by electrochemical reactions (1).

In batteries the chemical energy usually emerges from their limited amounts of metals, metal ions or oxides (1). In contrast to conventional batteries, fuel cells require hydrogen and oxygen to sustain the redox reaction and are therefore able to supply electrical energy over much longer time periods. For this reason fuel cells have been used for decades in space technologies and stationary fuel cells have been installed in utility power plants, hospitals, hotels, or office buildings. For the near future fuel cells represent also the new power source for the transportation sector.

The highest benefit over conventional combustionbased technologies is the high efficiency of up to 60 % (described as the ratio between the electricity produced and hydrogen consumed) as well as their climate friendliness (1). If pure hydrogen is used as a fuel, only heat and water are emitted as byproduct. Therefore fuel cells are considered to be smart, clean and efficient components to generate energy.

Although there are many types of fuel cells (as shown in Table 1) the basic components are very common: an anode, a cathode, and an electrolyte that allows ions to move between the two electrodes of the fuel cell. At the anode a catalyst causes the supplied fuel to undergo oxidation reactions that generate ions (H^+) and electrons. The H^+ moves from the anode to the cathode through the electrolyte, which can be a liquid or a solid. At the same time, the generated electrons flow from the anode to the cathode through an external circuit, directly producing electricity.

Fuel cells are classified by the type of electrolyte they use (see Table 1).

Fuel cell type	Electrolyte	Fuel	Oxidizer	Electrodes
Alkaline	NaOH; KOH	H ₂	O ₂	carbon support+ Ni, Zn or Al
Phosphoric acid	Phosphoric acid	H_2 with CO_2 traces	O ₂	carbon paper+ Pt particles
Molten carbonate	molten K-, Li -carbonate	H ₂ +CO mixture	O ₂	non-precious metals (Ni)
Solid oxide	ion- conducting oxide (zirconia treated with yttria)	H ₂ +CO mixture	O ₂	Cermet anode and lanthanum strontium manganite cathode
Proton- exchange membrane	ion- conducting membrane such as Nafion	H₂ or Methanol	O ₂	carbon support+ Pt particles

In this application report we will focus on catalytic material and ion-conducting membranes for protonexchange membrane fuel cells (PEMFC) whose major components are listed in Table 1. The PEMFCs have a quite broad range of applications due to their sufficiently low working temperature and quick start up

Table 1: Fuel cell types (1)



times. An exemplary model of PEMFC is depicted in Figure 1. The membrane typically consists of a carbon support, Pt particles, an ion-conducting membrane (e.g. Nafion ionomer), and/or Teflon binder.

The carbon support acts as an electrical conductor (allowing the passage of electrons) while the Pt particles act as catalytic reaction sites; the ionomer membrane provides the paths for proton conduction.

At the anode and cathode sites, the reactions are influenced by the catalytic action of platinum.

Figure 1 displays the reaction that occurs at the cathode: a catalyst promotes the reaction of ions (H^{+}) , electrons, and supplied oxygen (oxidizer) to form water or possibly other products (1).



Figure 1: Scheme of a proton-exchange membrane fuel cell (PEMFC); GDL: Gas Diffusion Layer, CL: catalyst Layer, Pt: Platinum____

In this report we demonstrate how the particle size, zeta potential and surface zeta potential give important information for the development and the production of catalytic material and ion conducting membranes with improved efficiency.

1.1 Particle size and zeta potential of carbon and carbon based catalyst

The Pt/C catalyst is combined with dispersing agent (e.g. surfactant), a binder and solvent to form the catalyst mixture, which is then used for the membrane coating. The particle size and zeta potential of the catalytic material must be controlled and optimized to form an adherent and continuous catalyst layer on the membrane. In the case of platinum on carbon (Pt/C) catalyst the particle size affects the interaction between catalyst and ionomer membrane, the thickness of the catalyst layer, the ionomer distribution, the oxygen diffusion and therefore also the final cell performance.

The carbon support (e.g. carbon black) is produced from small spherical particles (primary particles). During the production process or the catalyst formulation, they melt into particle aggregates and due to strong electric forces the aggregates remain closely bound, forming even large agglomerates with other aggregates (see Figure 2).



One parameter that affects the agglomeration behavior of particles is the zeta potential, which describes the surface charge of particles in a dispersant. The stability of colloidal dispersions can be estimated based on the zeta potential, i.e. based on the tendency of particles to repel each other. Dispersions with a highly negative (< -30mV) or highly positive (>+30 mV) zeta potential are referred to be stable.

So particle characterization and zeta potential are indispensable for quality control but also for development and analysis of catalyst formulations in order to create highly effective, stable, long lasting but also cheap products.

1.2 Zeta potential of ionomer membrane

The zeta potential analysis and determination of the isoelectric point (which is the pH values at which the zeta potential is 0 mV) of solid surfaces let us draw conclusions about surface functionalities or coating efficiency. For PEMFC electrodes it is highly important to reach long lasting maximum catalytic efficiencies. Therefore a catalyst/carbon support layer with a defined particle size and microstructure has to be evenly and stably attached to an electrolyte membrane (e.g. ionomer). The resulting thickness and uniformity (no irregularities) of the proton exchange membrane affect the H^+ passage and the consecutive reaction with oxygen and electrons (3).

We analyzed the surface zeta potential of catalyst coated membranes with different carbon contents in order to investigate the effect of carbon support on the coating.



2 Materials and Methods

Samples tested and corresponding instruments are listed in Table 2.

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Sample	Instrument & Technique	
Carbon black	Litesizer 500:	
Platinum on carbon (Pt/C) catalyst	 Particle size by DLS Zeta potential by ELS PSA: particle size by laser diffraction 	
 non – functionalized ionomer membrane catalyst coated ionomer membrane (high and low carbon content) 	SurPASS 3 : surface zeta potential by streaming potential)	

The particle size and zeta potential change over pH was investigated using the Litesizer 500. Tests were conducted in water and in 0.01 mol/l KCl solution. The latter was used to evaluate the effect of pH on the aggregates by using the same electrolyte solution as for SurPASS 3.

In fact the aggregate size of catalyst will affect the membrane coating and the resulting catalyst layer uniformity. A correlation between Litesizer 500 and SurPASS 3 data may provide additional information about the membrane structure. For the PSA (particle size analyzer), measurements were performed in water as dispersion medium.

2.1 Particle size by dynamic light scattering

The particle size analysis was performed using the Litesizer 500 equipped with the dosing unit accessory for automatic pH dependent titration. To optimize the sample dispersion 0.04 % Triton X-100 was used as surfactant both in the water and KCI solution. Before measuring the sample was further homogenized with a 200 W external sonicator (set at 90 % power). After 2 minutes the particle size did not show any further changes and a stable dispersion was reached. Measurements were conducted at 25°C in an Omega cuvette with the following settings: backscattering (175°), automatic filter, automatic focus mode, general analysis mode.

2.2 Particle size by laser diffraction

The PSA was used to measure the particle size distribution by means of laser diffraction. Given the volume of the liquid dispersion unit (400 ml) and different dispersion aids available in the PSA (stirring, sonication, pump), the sample dispersion conditions were adjusted from the ones used for the Litesizer 500.

The powder was directly dispersed into the liquid dispersion unit filled with 0.01 % Triton X-100. Since the maximum sonication power provided by the PSA is 50 W, samples were sonicated 30 min to completely stabilize the dispersion. Mie was selected as reconstruction mode and the refractive index of 2.4 with absorption index 0 was chosen. For the sample dispersion as well as the measurements itself (30 s measurement time) a medium stirrer speed (250 rpm) and a fast pump speed (300 rpm) were chosen.

2.3 Zeta Potential determinations by electrophoretic light scattering

Electrophoretic mobility measurements were performed in the Litesizer 500 using the dosing unit accessory for automatic pH dependent titration. Again the Omega cuvette and automatic power adjustments were selected. The measurements were performed at 25°C. The Smoluchowski approximation was used for the zeta potential calculation.

2.4 Zeta potential by streaming potential

The streaming potential measurements were conducted with the SurPASS 3 using the adjustable gap cell. For the measurement samples were fixed on sample holders with a cross-section of $20 \times 10 \text{ mm}^2$. The measurements were conducted by using a 0.01 mol/L KCI electrolyte solution.

The surface zeta potential change over pH was investigated to determine the isoelectric point (IEP). Moreover, the time dependence of the zeta potential was tested at pH 4 to evaluate the coating stability.

3 Results & discussion

3.1 Particle size distribution of carbon and Pt/C catalyst

Figure 3 shows the pH dependent alterations of the hydrodynamic mean diameter (HDD) for carbon and Pt/C catalyst in two different dispersants. In 0.01 mol/L KCl and pH < 5 carbon black shows a high tendency to agglomeration (HDD > 1 μ m). The aggregate size of Pt/C catalyst remains constant in the range of pH 3-7 (HDD \cong 0.3 μ m) in both media and is comparable to that of carbon in water.





Exemplary particle size distributions for both samples at pH 3.5 are visualized in Figure 4.

It can be observed how the size and the polydispersity index (PDI) for carbon increase dramatically while the Pt/C catalyst shows narrow particle size distributions and small size within the two dispersants. The Ptcoating in the Pt/C catalyst seems to decrease or suppress the pH- dependent formation of carbon agglomerates.



Figure 4: Exemplary intensity weighted particle size distribution for carbon black and Pt/C catalyst samples at pH 3.5 determined by DLS

The investigation of agglomerates was performed by using laser diffraction technology with the PSA.

The pH measured for the sample in the liquid dispersion unit was 6. Figure 5 displays the volume weighted but also the surface weighted particle size distributions of carbon black and Pt/C catalyst. By looking at the volume based distribution the mean diameter [4, 3] is significantly higher for the catalyst free carbon black which forms larger agglomerates. The broadness of the particle size distribution indicated by the span value is comparable between the two samples.



The surface based particle size distribution (PSD) provides information about the presence of the fine fraction, which contributes to the increase of the surface area. As expected, in the surface based PSD, the mean measured for carbon black is smaller (D [3, 2] =13.3 μ m) than the one measured in the volume weighted PSD (D [4,3]= 17.2 μ m) because the effect of smaller particles is more pronounced.

The increase of the surface area of the carbon support by means of the platinum particles allows enhancing the reaction rate and thus favors the catalytic activity (4).

3.2 Zeta potential of carbon and Pt/C catalyst

Figure 6 displays the pH dependent zeta potential values of carbon black and Pt/C catalyst in water and 0.01 mol/L KCl solution. For both samples in the two different dispersants the zeta potential magnitude decreases with decreasing pH. A more rapid decay occurs below pH 4.

A small magnitude of the zeta potential indicates that repulsion forces are less and particles start to agglomerate. This is confirmed by the particle size result in the section 3.1 where the tendency to agglomeration below pH 4 can be visualized especially for the carbon black.

Although a decreasing trend for the zeta potential is common to both samples, Pt/C catalyst shows a higher negative ZP (- 40 mV) in comparison with carbon black indicating a higher stability and the probability to form smaller agglomerates (see Figure 6). What can be also noted is that the zeta potential measured in KCl is always lower than the one measured in water for both samples. In fact, by increasing the ionic strength of the solution the electric double layer formed around the particle gets compressed leading to a decrease of electrostatic repulsion.

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3.3 Surface zeta potential of proton exchange

3.3 Surface zeta potential of proton exchang membranes

A non-functionalized ionomer membrane (reference) and catalyst coated membranes (with two different carbon contents) were characterized according to the surface zeta potential and IEP using streaming potential measurements.

Figure 7 shows the pH dependence of the zeta potential determined with the SurPASS 3. The IEP is shifted from pH 1.5 for the reference membrane to a higher pH 3.5-4 for the coated membranes. The zeta potential change indicates that the coating process occurred.



Figure 7: pH-dependence of the surface zeta potential for reference and coated membranes with different carbon contents

Moreover, the two coated membranes show a slight difference of the IEP. For the membrane with the lower carbon content (grey) the IEP occurs at slightly lower pH (3.5).

In this region, by looking at the Litesizer 500 data below pH 4, the aggregate size of Pt/C catalyst is

small (HDD \cong 0.3 µm). This shows that by performing the coating in this acidic region the final coating has a better uniformity. The uniformity of the coating affects the functionality of the catalyst layer. Figure 8 displays how the aggregate size of the coating will affect the oxygen diffusion through the membrane. In presence of small aggregates the Pt catalyst particles are more accessible to oxygen.



Figure 8: Schematic representation of the possible oxygen diffusion path in presence of small and large aggregates. Adapted from Wang et al. (2019) (2)

In a second measurement the stability of the catalyst coating in water at pH 4 was tested by the time dependence of the zeta potential (see Figure 9). The zeta potential shift of the coated membranes towards less negative values confirm the occurred coating. After 20 minutes equilibration time the membrane reaches a plateau which indicates the coating stability over time.







4 Conclusion

The efficiency of the proton exchange membrane in the fuel cell is strictly related to the particle size and stability of the catalyst. They affect the uniformity of the coating and thus the functionality of the resulting catalyst layer, which can be estimated by means of the surface zeta potential at the end of the coating process. In this application report we show how the aggregation and agglomeration process of carbon support and Pt/C catalyst can be investigated.

The Litesizer 500 equipped with the automatic titration unit allows monitoring the aggregate size and the corresponding zeta potential by different pH values. The choice of the right pH is crucial in the development of the catalyst because the success of the consecutive coating process is strictly related to the aggregate size distribution and to the stability of the catalyst at the chosen pH. Moreover, the zeta potential can be useful to estimate the electrostatic interactions existing between different components in the final catalyst formulation.

The catalyst contains aggregates which can be measured by the Litesizer 500 and agglomerates which are close to 10 μ m or larger. The latter undergo sedimentation during the measurement and therefore they cannot be detected during a DLS measurement. The large agglomerates can be measured using the PSA. Furthermore, the surface based PSD values provide additional information about the fine fraction content which contributes to increase the surface area.

Finally, the IEP shift and the surface zeta potential values measured by SurPASS 3 not only provide information about the coating but also show how the carbon content affects the membrane coating. The differences existing between the reference and catalyst coated membranes in terms of IEPs and zeta potential stabilization times are related to the aggregate and agglomerate size. Therefore, particle size, zeta potential and surface zeta potential can help in the development and in the manufacturing phase of proton exchange membranes for fuel cells.

5. References

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