Plasma-assisted synthesis of porphyrin-based catalysts

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Abstract: An RF discharge plasma is applied to enhance the electrochemical activity of porphyrin-based catalysts. The properties of catalyst are analyzed by cyclic voltammetry. Attenuated total reflection infrared spectroscopy and atomic force microscopy are applied to investigate the changes caused by plasma treatment. A correlation is found between the activity and morphology of the porphyrin nanoaggregates on the catalysts’ substrate.

Keywords: Low temperature plasma treatment; metalloporphyrins; catalysts; fuel cells.

1. Introduction
Plasma-assisted methods are widely used both for synthesis of ultrafine catalytically active particles or modification of catalysts [1-8]. Most of the conventional methods for preparation of catalysts include high-temperature calcinations/reduction or pyrolysis. Replacement of heat treatment step by low temperature plasma treatment minimizes some problem caused by high temperature such as aggregation, crystalline size grow and sublimation. The plasma prepared catalysts or catalysts modified by plasma exhibit a much higher activity, enhanced selectivity and better stability.

In this work we have used RF discharge plasma for synthesis of porphyrin-based cathode catalysts for the oxygen reduction reaction (ORR) in fuel cells.

2. Experimental

Materials. Commercial iron phthalocyanine bis(pyridine) complex (cat 1), phthalocyanine iron monochloride (cat 2), FeTFPPCl (cat 3), iron 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25 - hexadecachloro-29H,31H-phthalocyanine (cat 4), FeTMPPCl (cat 5) and CoTMPP (cat 6) were used as precursors of catalysts. Catalysts precursors were dissolved in THF, afterwards the mixture was added to a dispersion of the carbon support (Vulcan XC-72) in THF. Subsequently, the THF was removed and the impregnated carbon was plasma treated.

Plasma treatment. Plasma treatment was performed in inductively coupled radio frequency (RF) plasma generated in a vibrating bed reactor. The reactor is described in detail elsewhere [3]. The plasma was generated by inductive coupling from a copper coil into the reactor through the quartz glass window. The samples were located on the holder at the distance of 900 mm (position 1) or 120 mm (position 2) from the window. The experiments were carried out in Ar, Ar:O2 and N2 at pressure of 10 Pa. The plasma power was 150 W. The plasma treatment time was 30 min.

Characterization. Cyclic Voltammetry was carried out to test the catalysts activity towards ORR. An O2-saturated H2SO4 solution was used as a electrolyt. The current density (J) at 0 V vs Ag/AgCl was chosen as a measure of catalytic activity. Attenuated total reflection infrared spectroscopy (ATR-IR) and Atomic Force Microscopy (AFM) were used to characterize the morphology of samples before and after plasma treatment.

3. Results and Discussion
Electrochemical activity. Fig.1 shows the effect of plasma treatment on the electrocatalyst activity.

![Fig.1](image-url)

Fig.1 Electrochemical performance of porphyrin-based catalysts after plasma treatment in different gases at different positions in the reactor. The catalyst load was 50 wt%.
The current density at 0 V vs Ag/AgCl was chosen as a measure of electrocatalytic activity. It is clearly visible that there was a strong effect of the plasma treatment on catalyst performance. The maximal value of current density, $J_{\text{max}}$, of 2 mJ cm$^{-2}$ was observed for catalysts 2 and 3.

Fig. 2 shows the effect of plasma treatment on the improvement of the electrocatalyst activity.

The improvement of the activity ($\Delta J$) is derived from the formula:

$$\Delta J = \frac{J_{\text{cat}} - J_{\text{untreated}}}{J_{\text{untreated}}} \cdot 100\% - 100\% \quad (1)$$

Plasma treatment induced different effects depending on the catalysts precursor. For treatment position 1, a positive effect of Ar plasma treatment on the catalysts activity was achieved for cat 4 and, in a less degree, for cat 1 and 6. Treatment of catalysts in Ar plasma at position 2 improved the performance of all catalysts, excluding the cat 1. The best improvement in activity was achieved for cat 3. N$_2$-Plasma treatment resulted in increase of activity of catalyst 4 irrelevant of the position in reactor.

Catalyst 4 was chosen for further detailed characterization.

Catalysts characterization. Atomic force microscopy (AFM) was used to investigate the morphology of both untreated and plasma treated catalysts. For AFM investigations, catalyst precursor solution was deposited on the glass plate. The surface of the glass plate was covered with carbon (amorphous hydrogenated carbon, a-C:H) film to simulate the real surface of catalyst.

Fig. 3 shows the typical AFM images of the structures formed from the catalyst precursors on the glass plate covered with a-C:H film. Three different structures were observed: rings, star-like structures and semispherical particles. These structures were the results of the two competing process: self-assembly of the porphyrin molecules inside the liquid and evaporation of the solvent.

Rings formation was observed on the surface of the catalysts 3, 5 and 6. The rings were 40-80 nm high above the glass plate surface.

(a) Cat 1  (b) Cat 2  
(c) Cat 3    (d) Cat 4  
(e) Cat 5    (f) Cat 6

Fig. 3. AFM images (10 x 10 µm) of untreated catalysts on the glass covered with a-C:H film.
The average height of the rings, however, depends on the concentration of solution with smaller height formed at lower concentration. The rings with height of 5 nm were observed when deposited from the solution with a concentration of $10^{-5}$ M. The ring diameters were found to be in the range of 1-2 µm.

Two mechanisms were proposed for ring formation processes, the pinehole mechanism [9-11] and coffee-stain mechanism [9,12-14]. During self-assembling of the porphyrin molecules in the solution, liquid film thickness is continuously reduced via evaporation. According to the pinehole mechanism, formation of the holes in the thinning liquid layer leads to the ring formation. When holes open the self-assembling structures are pushed away and collected in the inner perimeter of the hole. After the evaporating process is completed, the solute is deposited as rings. Rings thus formed are expected not to contain any particles inside. The coffee-stain mechanism explains the formation of the rings from solution droplets. During evaporation of the liquid, the dispersed material is transferred from the interior to the edge of the drop. If the material is not transferred completely, the particles can be formed inside the rings.

Though almost every ring of cat 6 had one large particle on its end, no particles were observed inside the rings. It implies that the rings were formed by pinhole mechanism.

(a) 10 x 10 µm        (b) 10 x 10 µm

(c) 5 x 5 µm          (d) 5 x 5 µm

Fig.4. AFM images of untreated (a, c) and treated (b, d) catalysts on the glass covered with a-C:H film.

No correlation was found between the ability of porphyrin molecules to form the rings and their electrocatalytic activity.

Fig.4 shows the changes in the morphology of the catalysts after Ar plasma treatment. The images of untreated catalyst (Fig.4 a and c) show the areas with a few isolated rings with diameters from a few hundred nanometers to somewhat less than 2 µm. No particles were observed on the surface of catalyst. As it can be seen from the Fig. 4 b and d, plasma treatment resulted in distraction of the rings. New spherical particles were observed on the catalysts’ surface.

The enhancement in catalytic activity was likely due to the distraction of ring-shaped assemblies and formation of new smaller spherical nanostructures on the surface of catalysts.

![Fig.5. Selected line scans in the topographic images shown in Fig. 4 (c, d).](image)

The line scan analyses of the AFM images Fig. 4c and d are shown in Fig. 5 a and b correspondently for the lines drawn through the edges of the larger ring. From this graph it is clearly visible that plasma treatment resulted in a decrease of the ring rims. The height of the ring rim was found to decrease up to 30%.

Attenuated total reflection infrared spectroscopy (ATR-IR) spectroscopy was applied to follow the changes in porphyrin structure after plasma treatment.

Fig. 6 shows the ATR-IR spectrum of the pure FeTFPPCI (precursor for cat 3) in the region 650 –4000 cm$^{-1}$.

The ATR-IR spectra of the catalysts treated under different conditions are shown in Fig. 7. In order to pro-
vide a basis for comparison, the spectra for pure untreated FeTFPPCl (precursor for cat 3), untreated mixture of Vulcan and FeTFPPCl (untreated cat 3), and Vulcan (support for cat d) are also given.

Fig. 6. ATR-IR spectrum of pure untreated FeTFPPCl.

Fig. 7. ATR-IR spectra for Vulcan (a), untreated cat 3 (b), Ar:O₂ plasma treated cat 3 (c), N₂ plasma treated cat 3 (d), Ar plasma treated cat 3 (e) and pure untreated FeTFPPCl (f).

No drastic changes in the spectra were observed. Though, in should be noted that the bands between 1500 and 930 cm⁻¹ became broader.

4. Summary

Our contribution shows the potential of a plasma treatment in the preparation of noble metal free electrocatalysts for the oxygen reduction reaction in the fuel cells. The large differences in catalytic activity of porphyrin-based catalysts were observed, depending on the plasma treatment applied to the catalysts during their preparation. The electrochemical activity, expressed in terms of the current density at v vs. Ag/AgCl, was up to 30% higher for plasma treated samples than that for untreated. The enhancement in catalytic activity was likely due to the distraction of ring-shaped assemblies of porphyrin molecules and formation of new smaller spherical nanostructures on the surface of catalysts.

References