



Stability of carbon nanofibre-supported platinum catalysts in the presence of chloride under controlled mass-transfer conditions



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HIGHLIGHTS

- Platinum catalysts were supported on carbon nanofibres.
- Chloride ions cause significant degradation during potential cycling.
- The main cause for the degradation is a decrease in the number of platinum particles.
- The degradation rate is dependent on the rotation rate.

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ABSTRACT

The effect of chloride on the stability of platinum electrocatalysts was studied by rotating disk measurements in sulfuric acid electrolyte with a continuously increasing concentration of chloride anions. The activity towards oxygen reduction was found to be reduced by a factor of seven when 140 ppm chloride was present. Platinum corrosion was severe at high potentials, presumably accelerated by potential cycling, and greatly enhanced by mass transport. A five-fold increase in corrosion rate was found when the electrode was rotated at 1600 rpm with respect to stagnant conditions. At potentials where oxygen reduction occurs, dissolved Pt can be redeposited on the electrode. The Pt dissolution rate increased with increasing Cl^- concentration up to 20 ppm. Above this threshold the corrosion rate was unaffected by increases in Cl^- content.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are attractive low-emission power sources for electric propulsion vehicles [1]. When supplied with hydrogen produced from renewable energy sources such as wind or solar energy, they have the potential of producing electricity without other emissions than water. Although the technology has come far, and automobile manufacturers and fuel cell developers have produced PEMFC vehicles for years, two major challenges remain: cost and lifetime [2].

Several factors can reduce the lifetime of the fuel cell, including platinum-particle dissolution and agglomeration, carbon support

corrosion and membrane thinning. Additionally impurities, either from fuel or air can accelerate degradation. Typical fuel impurities include CO , CO_2 , NH_3 and H_2S originating from reforming of hydrocarbons. NH_3 and H_2S are critical impurities, as irreversible degradation occurs [2]. Traces of ammonia can be formed in natural gas-reforming processes, and levels as low as 10 ppm can seriously impact the performance [3]. Long-term exposure can give irreversible reduction in performance. Impurities originating from air supply to the cathode can be SO_2 , NO_2 , H_2S and NO , and have been reported to give irreversible damage to PEMFC [4–7].

Anionic impurities can be introduced to the membrane electrode assemblies (MEA) from water-cooling systems/humidifiers or as residual from catalyst production. When fuel cells are used in road transportation, saline air or de-icing of roads may be an anion source [2]. Matsuoka et al. [8] investigated the impact of Cl^- , F^- , SO_4^{2-} and NO_3^- on fuel cell performance. It was found that only chloride had a negative effect on the fuel cell voltage during operation. A platinum loss of 30% after 50 h operation was reported.

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Several authors have shown increased degradation rates of fuel cell electrocatalysts in the presence of chloride impurities. Mitsuhashi et al. [9] studied the solubility of Pt in different electrolytes. They found a much higher concentration of dissolved Pt when Cl^- was added. A linear dependency on the Cl^- concentration up to 2.8 mM was found. The increased solubility was attributed to the presence of chloride complexes. In the work of Yadav et al. [10], the effect of Cl^- on electrodeposited Pt was studied with an electrochemical quartz crystal microbalance (EQCM). The loss of Pt was suggested to be caused by the following reactions [11,12]:



The degradation appeared to be relatively insignificant below 100 ppm. However, for nanosized Pt particles the corrosion rate can be significant, as was shown by our electrochemical quartz crystal microbalance (EQCM) [13] in which an electrode made from a fuel cell catalyst (50 wt.% Pt/C) lost 10% of its platinum content over a 24 h period when exposed to a sulfuric acid solution containing 10 ppm of chloride and at a constant potential of 1.2 V vs. a reversible hydrogen electrode (RHE). Li et al. [14] investigated the effects of trace amounts of chlorine in PEM fuel cells to address the possibility of using hydrogen from the chlor-alkali industry as a fuel in PEM fuel cells. In line with our results [13], Li et al. [14] also found a significant, non-recoverable loss in electrochemical surface area (ECSA). This group later investigated the loss of ECSA in catalysts of fuel cell catalysts (46 wt.%) by the use of EQCM and found losses of 4%, 7% and 13% during 1000 potential cycles at a rate of 50 mV s^{-1} from 0.4 V to 1.2 V in 500, 1000, and 2000 ppm, respectively [15]. The duration of these experiments is therefore much shorter than those in Ref. [13], and a direct comparison is difficult. However, the almost instantaneous 50% loss even at 50 ppm in Ref. [13] would seem to indicate that chloride is more aggressive during potentiostatic hold than during cycling. Later results in a PEM fuel cell appears to indicate that also the mass transfer is affected by chloride contaminations [16]. A related result was found by Baturina et al. [17], who found that the presence of HCl during fuel cell operation influenced also the part of the polarization curve dominated by the diffusion of molecular oxygen. The effect of mass transport on degradation rate, on the other hand, is to our knowledge not yet reported.

The presence of chloride may also affect rates of the fuel cell reactions themselves. Schmidt et al. [18] studied the oxygen reduction reaction on a carbon supported Pt fuel cell catalyst in the presence of different anions and found that the oxygen reduction reaction (ORR) activity decreased in the order $\text{ClO}_4^- > \text{HSO}_4^- > \text{Cl}^-$. The results were similar to those for smooth polycrystalline and single crystal Pt electrodes, and consistent with the increasing adsorption bond strength of the anions. Enhanced formation of H_2O_2 in the presence of Cl^- was also encountered in these experiments, and the need for chloride free electrode preparation schemes in order to avoid performance losses and/or corrosion/degradation effects was stressed. Similar results were reported by Baturina et al. [17].

Replacing the classical carbon-black supports such as Vulcan XC-72, may influence the catalytic activity significantly [19–23]. For example, we recently showed that there is a significant gain in terms of the activity for the methanol oxidation reaction if XC-72 is replaced by carbon nanofibers [24]. It therefore becomes of significance to investigate the stability of catalyst deposited on such supports with relevant impurities present in the fuel.

Below we present results demonstrating the effect of mass transfer on Pt-dissolution and the oxygen-reduction reaction at a

carbon nanofibre-supported Pt catalyst for PEM fuel cells. For our studies we employed a controlled, continuous release of Cl^- from a Saturated Calomel Electrode (SCE) reference electrode to quantify the influence of Cl^- on the Pt corrosion. We thus also show how to extract data for chloride-induced dissolution of Pt under continuously changing concentrations of the chloride, which may be methodologically useful in corrosion studies of PEM fuel cell catalysts.

2. Experimental

A modified polyol method [25,26] was used for preparation of a 10 wt.% Pt catalyst on platelet carbon nanofibre support. 200 mg of carbon was dispersed in 50 ml of ethylene glycol (VWR, AnalaR NORMAPUR™). The suspension was ultrasonicated for 30 min. After the ultrasonic treatment, 50 ml of a precursor solution (H_2PtCl_6 (VWR) in ethylene glycol) corresponding to 10 wt.% nominal loading and 0.4 g of NaOH (Alfa Aesar p.a) was added. The mixture was heated and kept at 160°C for 1/2 h under Ar atmosphere before cooling to room temperature. 100 ml of de-ionized water was added and the sample allowed to settle to sedimentation for 6 h. The resulting catalyst was filtered and washed thoroughly with de-ionized water and dried.

Thin film electrodes were prepared by a procedure described by Schmidt et al. [27] and Paulus et al. [28]. In short, 20 μl of a slurry containing 1 mg catalyst per 1 ml of a 20% isopropanol in water solution was pipetted on to the disk of a rotating ring-disk electrode (RRDE, Pine). After drying under Ar, 20 μl of a Nafion solution (Alfa Aesar 5% w/w) diluted 1:100 with water was applied to the electrode, forming a thin Nafion film after water evaporation.

Electrochemical experiments were performed in a three electrode setup using an SCE (Pine Instruments) or a Reversible Hydrogen Electrode (RHE) as reference electrode placed directly into the solution. However, all potentials are reported vs. RHE. A Pt wire enclosed in a separate compartment with a glass sinter separator was used as counter electrode, except for the measurements involving ICP for which a Pd wire was employed. All measurements were conducted in a 0.5 M H_2SO_4 (Merck, p. a.) electrolyte saturated with oxygen (AGA, 5.0). All glassware in contact with the electrolyte was carefully cleaned by boiling in a solution of 71 vol. % de-ionized water, 28 vol. % H_2O_2 (35%) and 1 vol. % concentrated H_2SO_4 in order to remove organic impurities.

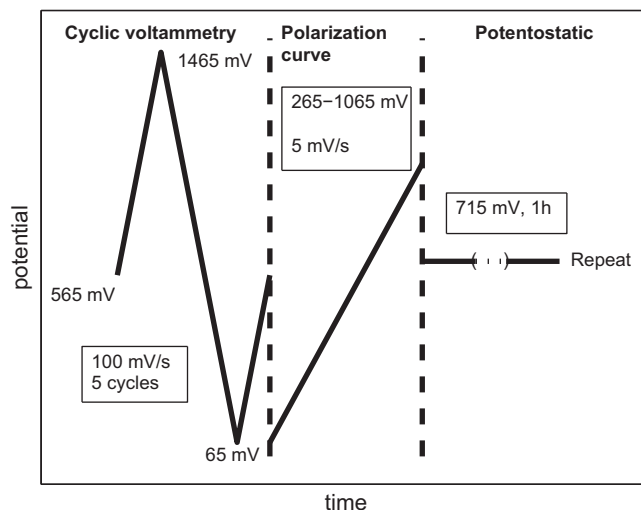


Fig. 1. Electrochemical test procedure.

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