



# On the oxygen reduction reaction in phosphoric acid electrolyte: Evidence of significantly increased inhibition at steady state conditions



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## ABSTRACT

In the presented work, we investigate the oxygen reduction reaction (ORR) in half-cell measurements employing different electrolytes. The aim is to compare the ORR inhibition due to anion adsorption at transient as well as steady state conditions. It is found that the ORR inhibition at the platinum – phosphoric acid electrolyte interface is a relative slow, time dependent process. The major inhibition is not observed in transient polarization curves but only under steady state conditions. This observation is in contrast to the typical ORR inhibition due to anion adsorption as observed for example in sulfuric acid electrolyte. In sulfuric acid the inhibition is fast and then stays more or less constant in time. As a consequence of our findings, common transient measurements of the ORR activity might not be sufficient to investigate suitable mitigation strategies for the ORR inhibition in phosphoric acid electrolyte. Such strategies need to take steady state conditions into account.

In order to explain the slow ORR inhibition in phosphoric acid electrolyte, two possible explanations are discussed. Either the adsorption of phosphate is a slow, complex process, where a fast adsorption step is followed by a consecutive filling of the surface, or a mass transfer barrier develops at the polarized phosphoric acid–electrode interface. The latter might be the viscoelectric effect that is known from colloidal science.

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## 1. Introduction

The electrochemical interface and specific anion adsorption on metal surfaces are subject to numerous studies regarding their influence on electrocatalytic reactions, see for example refs. [1–14] for an overview. Most studies are related to surface science and therefore target the structure sensitivity of anion adsorption on well-defined single crystal surfaces. For the oxygen reduction reaction (ORR) on Pt, it was for example shown that not only electronic and geometric properties determine the ORR activity [15,16], but the structure sensitive anion adsorption leads to the blocking of reaction sites, therefore severely inhibiting the reaction for specific surface geometries [4–6,17–20]. In other words, the structure sensitivity observed for the ORR, is not only due to a structure sensitive ORR process, but also due to structure sensitive

anion adsorption. In this respect, the site blocking model gave a very elegant explanation for the different order in ORR activity when comparing low index Pt single crystal surfaces in sulfuric acid and perchloric acid electrolyte, respectively [1]. In addition it could explain the positive effect of adsorbed cyanide anions on the ORR activity in sulfuric and phosphoric acid electrolyte [21]. However, so far the experimental investigations have been performed under transient conditions, i.e. cycling the electrode potential. It is assumed that the adsorption process is fast and that therefore the anion coverage on the electrode always is in equilibrium [22]. To the best of our knowledge no previous investigations of the time dependence of these processes were performed that highlight the significant differences between the behavior of sulfuric and phosphoric acid. In contrast in general it is assumed that anion adsorption from phosphoric and sulfuric acid act similar, while perchloric acid exhibits only weak or no blocking [1,2,23–27].

Anion adsorption has also severe practical consequences in electrocatalysis, e.g. for phosphoric acid based fuel cells. Phosphoric acid fuel cells (PAFCs) were the first commercially successful fuel cells, but never entered the mass market due to their high

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costs. However, PAFCs gained renewed interest with the invention to embed the liquid acid electrolyte in a matrix of polybenzimidazole (PBI) [28]. This type of fuel cell is now typically referred to as high temperature proton exchange membrane fuel cell (HT-PEMFC) [29,30]. The higher operating temperature of HT-PEMFCs as compared to low temperature (LT) PEMFCs has several advantages. For example it provides a higher CO tolerance and produces water vapor instead of liquid water as product. Yet the reaction rate of the ORR is significantly lower than expected from the high operation temperature. This inhibition of the ORR rate represents one of the major hurdles for the economic success of HT-PEMFCs. Often it is associated with the same site blocking mechanism observed in electrochemical half-cells, where the phosphate anions completely block the active sites of Pt. Alternatively – or in addition – the low solubility of oxygen in concentrated phosphoric acid was highlighted to explain the poor performance [30–35].

Studies using in electrochemical half-cells to investigate possible mitigation strategies for the ORR inhibition in phosphoric acid are in general performed at transient conditions. In the presented work, we scrutinize the underlying phenomena of the poor performance of HT-PEMFCs by investigating the time dependent influence of different anions on the ORR. In contrast to previous measurements we concentrate on the steady state behavior in different acidic electrolytes. The main aim is to show that in contrast to previous assumptions there is a considerable difference between the site blocking in sulfuric acid electrolyte and the inhibition observed in phosphoric acid.

## 2. Experimental

All electrochemical measurements were conducted in an in house developed three-compartment electrochemical cell made out of Teflon [36,37]. A saturated calomel electrode (SCE), separated from the working electrode compartment by a membrane, was used as the reference electrode [38]. However, all potentials in this study refer to that of the reversible hydrogen electrode (RHE), which was experimentally determined by measuring the hydrogen evolution (HER) and hydrogen oxidation reaction (HOR). All electrolyte solutions, i.e. 0.1 M HClO<sub>4</sub>, 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.75 M H<sub>3</sub>PO<sub>4</sub> were made with Suprapure grade chemicals and Millipore water (Resistivity = 18.2 MΩ cm, TOC < 5 ppb). For experiments in 0.1 M HClO<sub>4</sub> with varying amounts of H<sub>3</sub>PO<sub>4</sub>, 0.5 M H<sub>3</sub>PO<sub>4</sub> was added to the 0.1 M HClO<sub>4</sub> electrolyte until the desired concentration was reached. In all measurements the electrolyte was constantly purged by Ar, H<sub>2</sub>, or O<sub>2</sub>.

The working electrode was a polycrystalline (PC) Pt disk ( $\varnothing = 5$  mm,  $A = 0.196$  cm<sup>2</sup>) mounted into the tip of a rotating disk electrode (RDE; Radiometer Analytical). The counter electrode was a Pt mesh. As only trends are investigated, all currents in this study are given in terms of geometric current densities (mA cm<sup>-2</sup>) and all experiments were performed at room temperature. The roughness factor (ratio between real and geometric surface area) of the Pt electrode is around 1.7–1.9. The solution resistance was online recorded with the potentiostat (ECi-200 Nordic Electrochemistry) by superimposing a 5 kHz, 5 mV AC signal and compensated for by an analogue positive feedback scheme [39]. The effective solution resistance was around 2Ω. The stripping procedure we employed for some of the experiments is explained in detail in previous work [40]. In short, in the automated measurement sequence (Software from Nordic Electrochemistry) we applied a voltage profile consisting of holding the potential for 100 s at a certain start value followed by recording a single cyclic voltammogram with a sweep rate of 500 mVs<sup>-1</sup>. After the sweep a potential hold at the next potential value was applied. The current density measured at

each potential hold after 100 s applying a rotation rate of 1600 rpm is referred to as the steady state current density.

## 3. Results and discussion

As discussed in the introduction, the aim of this work was to study the time dependent influence of anion adsorption on the ORR at the Pt electrolyte interface with different electrolyte solutions. We start the discussion of our results with the basic electrochemical behavior of Pt in the three Ar saturated electrolytes 0.1 M HClO<sub>4</sub>, 0.05 M H<sub>2</sub>SO<sub>4</sub>, and 0.75 M H<sub>3</sub>PO<sub>4</sub> solution. We chose these concentrations in order to adjust all electrolytes to approximately pH 1; pH values of 1.10 (HClO<sub>4</sub>), 1.27 (H<sub>2</sub>SO<sub>4</sub>), and 1.05 (H<sub>3</sub>PO<sub>4</sub>) were determined by the measured potential of the reversible hydrogen reaction (HER/HOR) versus the SCE reference electrode.

In Fig. 1, polarization curves of Pt in contact with these electrolytes are shown. The start potential was held for 100 s at 1.1 V<sub>RHE</sub> and thereafter a single cyclic voltammogram was recorded—a procedure we previously dubbed as stripping procedure [40]. The obtained curves display the well-known behavior of Pt in these electrolytes. Taking the polarization curve recorded in 0.1 M HClO<sub>4</sub> as example, starting from 1.1 V<sub>RHE</sub> and scanning in negative direction, a peak at around 0.8 V<sub>RHE</sub> is seen, which usually is ascribed to the reduction of oxygenated species such as Pt-OH<sub>ad</sub> and Pt-O<sub>ad</sub> formed during the potential hold. In the adjacent potential region between 0.6 and 0.4 V<sub>RHE</sub> only capacitive currents from the double layer discharge are observed, while between 0.4 to 0.05 V<sub>RHE</sub> two peaks due to hydrogen underpotential deposition (H<sub>upd</sub>) arise. In the subsequent positive scan, the H<sub>upd</sub> desorption and double layer charging processes give rise to anodic currents that are largely symmetrical to the respective cathodic process. By contrast, the formation of Pt-OH<sub>ad</sub> and Pt-O<sub>ad</sub> occurs at different potentials in the positive and negative going sweeps, and thus often is dubbed as irreversible.

Comparing the behavior of Pt in the three different acid electrolytes, the same peak positions for the reduction of oxygenated species are observed. Slight differences in the peak area indicate that a different amount of oxygenated species has been formed in each electrolyte. This is in line with the onset potential for the Pt-OH<sub>ad</sub> formation found in the positive going scan. In perchloric acid electrolyte Pt-OH<sub>ad</sub> formation starts at slightly lower potentials as compared to the other two electrolytes. The H<sub>upd</sub> process displays an electrolyte dependent behavior as well. Unlike in HClO<sub>4</sub> solution, the H<sub>upd</sub> peak at around 0.3 V<sub>RHE</sub> gets more pronounced in H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> based electrolyte. It is

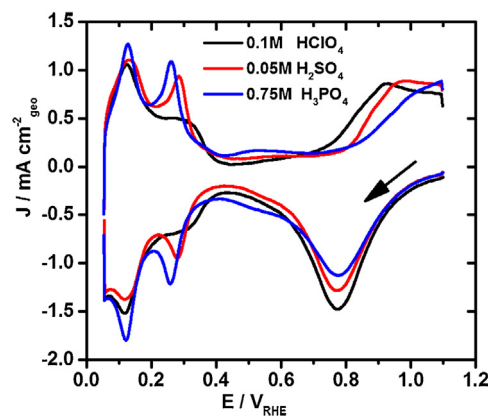


Fig. 1. Polarization (stripping) curves recorded after potential hold for 100 s at 1.1 V<sub>RHE</sub> in Ar saturated 0.1 M HClO<sub>4</sub>, 0.05 M H<sub>2</sub>SO<sub>4</sub>, and 0.75 M H<sub>3</sub>PO<sub>4</sub> electrolyte respectively. All solutions have pH 1. The scan rate was 0.5 V s<sup>-1</sup>.

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