Reactive oxygen species formation at Pt nanoparticles revisited by electron paramagnetic resonance and electrochemical analysis

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ABSTRACT

A combined electrochemical and electron paramagnetic resonance (EPR) procedure for the study of oxygen reduction reaction (ORR) intermediates generated at Pt nanoparticles (NPs) is validated in this work. Using spin-trap EPR complemented by electrochemical analysis, we show that we can detect and identify the free radicals that are produced during the ORR through trapping with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) which are otherwise difficult to detect. Experiments with 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline-N-oxide (DEPMPO) as spin trap show no evidence of DMPO-OOH and indicate that only OH radicals are trapped during the ORR. The results of this study serve as a functional proof-of-concept for further research on the identification of radical ORR intermediates in solution. We propose that our procedure can be used for a more rigorous quantification of free radicals involved in other electrochemical reactions.

1. Introduction

The loss of electrochemical active surface area (EASA) and degradation of the proton exchange membrane are two major problems plaguing the cost-effectiveness of Pt nanoparticles (NPs) for use as electrocatalysts in proton-exchange membrane fuel cells (PEMFC) [1,2]. It has been proposed that both problems may be caused by the presence of free reactive oxygen species (ROS) in solution, which cause Pt dissolution and attack the carbon support [3–6]. These free ROS are the desorbed intermediates from the ORR that takes place at the surface of the NPs. Numerous studies have attempted to shed light on the ORR mechanism in acidic conditions, often with conflicting conclusions [7–9]. Electrochemical studies typically employ surface analysis techniques to investigate the adsorbed intermediates or make use of the rotating ring disk electrode (RRDE) technique to study the desorbed intermediates in solution [10,11]. Literature on fuel cell technology generally focuses on membrane degradation using commercial catalysts and cites hydroxyl radicals (‘OH) as the responsible intermediates [12,13]. This is due to evidence of ‘OH formation at both anode and cathode [14,15], as well as its strong oxidative properties compared to superoxide (O2•) and hydroperoxyl (‘OOH) [16].

Free radicals are difficult to detect directly due to their short lifetime and high reactivity. A common technique for detecting radicals is electron paramagnetic resonance (EPR) spectroscopy [12,13,17]. EPR is used to investigate compounds containing unpaired electrons, such as organic radicals and paramagnetic transition metal ions and complexes. A variety of electrochemical processes has been studied using EPR, such as reactions in fuel cells [12], organic syntheses [18], and Li-ion batteries [19,20]. However, EPR is not as common as other spectroscopic techniques used in spectroelectrochemistry because of cell size limitations, high dielectric loss due to the electrolyte, and possible reflectance and absorbance of microwaves by the electrode material [21]. Long-lived paramagnetic species can be monitored directly, whereas short-lived species either require a continuous high rate of production or stabilization via spin traps to be detected. Spin traps are often nitro-based molecules that bind to the radical to form a longer-lived radical adduct. EPR studies on the ORR or fuel cell membranes typically use 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) for trapping, which readily binds to ROS and yields distinctive spectra that allow for easy identification [1,12].

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We believe this is the first approach that combines electrochemical analysis and EPR spectroscopy to investigate soluble radical intermediates produced during the ORR on electrodeposited Pt NPs. In this communication, we propose and validate a procedure using ex situ EPR complemented by electrochemical analysis to detect, identify and semi-quantify the produced radicals. Relating the charge consumed during the electrochemical reaction with the intensity of the observed EPR signal is a starting point to better quantify the free radicals produced in the reaction. This approach will be further developed to allow us to investigate the ORR mechanism through the identification of the soluble intermediates and may be expanded to other electrochemical processes where identification and quantification of radical intermediates is important. With this methodology, we hope to contribute to the elucidation of the ORR mechanism on nanoporous Pt NPs. A better understanding of the ORR in liquid electrolyte may help improve understanding of the ORR in fuel cell applications as well.

2. Materials and methods

The electrochemical experiments were carried out in a standard three electrode setup in 0.1 M HClO₄ electrolyte prepared from concentrated HClO₄ (Sigma) and Millipore water. DMPO (TCI Chemicals) was added to the electrolyte as a spin trapping agent at the start of each chronoamperometry (CA) experiment. For ORR measurements, the electrolyte was saturated with O₂ before and during the CA experiments by bubbling pure O₂ through solution. For the deoxygenated CA experiments, the electrolyte was purged with N₂ instead of O₂ before and during electrolysis. All CA experiments were performed at 0.5 V vs. Ag/AgCl near the onset potential of the ORR. This work is intended as a proof-of-concept for the (semi)quantitative correlation between EPR and electrochemical data. In ongoing experiments, the reaction is being expanded to a flow setup. Custom working electrodes with a large surface area were constructed by embedding a vitreous carbon disk in an epoxy resin and...
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milling it in a cylindrical shape. This was necessary to generate enough radicals to capture and detect via spin trapping EPR spectroscopy. Nanoporous Pt NPs were deposited on the carbon surface via a double pulse electrodeposition process [22]. This procedure was chosen for several reasons. Pt NPs exhibiting nanoporosity have been reported to have high catalytic activity towards the ORR [23–25]. These particles are sensitive to degradation, possibly due to Pt dissolution [26], making them ideal for our study. Secondly, the procedure ensures that all the electrocatalytic material is located in areas accessible during the ORR. Admittedly, these particles are of a greater size than normally used in fuel cells but are suited for this study for ease of preparation and visual analysis through SEM. Nine electrodepositions were prepared according to the same procedure and used as working electrodes. The particle size, distribution and surface coverage were determined according to the same procedure and used as working electrodes. The particle size, distribution and surface coverage were determined according to the same procedure and used as working electrodes.

Before every CA experiment, a cyclic voltammetry (CV) experiment was performed as a surface cleaning pre-treatment in 0.1 M HClO4. A Pt mesh was used as the counter electrode. Information) . A saturated Ag/AgCl electrode was used as a reference and only showed a DMPO-OH signal. A typical experimental spectrum and simulation are shown in Fig. 1d. Despite our high electrode surface area and averaging over multiple single EPR sweeps, some spectra still show a low signal-to-noise ratio. In order to avoid offsets due to the noise, each spectrum was first simulated. This spectrum was then double integrated and normalized to the EASA, the result of which is referred to as the EPR intensity DI in Figs. 2 and 3 and related discussions.

### 3. Results and discussion

Fig. 2a shows a plot of the EPR intensity DI versus time for three electrodes performed in oxygenated electrolyte. As the experiments progress over time, the average EPR intensity DI of the DMPO-OH signal becomes stronger. The biggest increase is observed after the first five minutes, after which the intensity slowly increases for some electrodes or stays constant for others. The increase in EPR intensity DI is consistent with the increase in consumed charge Q, as is evident from Fig. 2b, which shows a plot of the charge Q passed during the ORR over time as calculated according to Fig. 1b. In experiments where the increase in consumed charge is greater, the EPR intensity DI is also greater, with the exception of PtNP9. Fig. S2 shows the particle size distributions for all

![Fig. 2. Plots of (a) the average EPR intensity DI and (b) the average charge Q and versus time. PtNP3 (green), PtNP4 (cyan) and PtNP9 (dark blue) correspond to the experimental results of three of the electrodeposited electrodes. Error bars are normal standard error, with N = 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
electrodepositions. Despite some variations in particle size distributions and surface coverage, we can distinguish no relationship between particle size distribution and the EPR intensity DI or consumed charge Q. This would imply that the rate of radical desorption and spin trapping are independent of the morphology of the electrode within the morphologies that we studied.

We performed control CA experiments in deoxygenated electrolyte to check that the •DMPO-OH signal indeed originates from the trapping of free ORR radicals, and not from an electrochemical reaction of DMPO on the electrode surface. No EPR signal was observed in absence of dissolved oxygen. Initial experiments were performed at lower potentials more favorable for \( \text{H}_2\text{O}_2 \) production and yielded false-positive results due to Fenton side reactions with iron ions that was present in the initial system. We would like to stress the importance of avoiding any iron-based substances, such as Hamilton needles, to prevent such mishaps.

Fig. 3 shows the EPR intensity DI versus the charge Q of the oxygenated CA experiments shown in Fig. 2 a and b for all nine electrodes that were used in this study. The results were fitted with a linear fit. A linear relation between consumed charge and EPR intensity DI is observed that is consistent over time. We can thus conclude that the number of radicals produced during the ORR is directly proportional to the charge that is measured. The relation does not appear to be influenced by the morphology of the electrodeposited electrode within the studied NP distributions, nor by the electrochemical active surface area shown in Fig. S4. We hope to expand our study in the future with different electrodeposited electrode morphologies, commercially available electrodes and the effect of potential and electrolyte pH.

So far, our combined electrochemical and EPR procedure allows for the detection of ORR radicals, but does not directly distinguish between different intermediates due to the fast decay of •DMPO-OOH and the poor 'OOH trapping kinetics (Fig. 1a). •DMPO-OOH would only be detected if the rate of ‘OOH production was high enough, which does not appear to be the case for our system. However, this problem can be circumvented through use of a different spin trap: 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline-N-oxide (DEPMPO). DEPMPO is a suitable spin trap for ROS but is slightly more reactive towards •OOH than DMPO (Fig. 4a) [34]. In addition, the decay of •DEPMPO-OOH to •DEPMPO-OH is much slower: ±20 min in acid medium [35]. This is sufficiently large for the time frame of our measurements. Like DMPO, DEPMPO appears to be electrochemically inert within the electrochemical window of our experiments (see Fig. S4) [27]. Prior to the CA experiment, 10 mM DEPMPO was added to the electrolyte instead of DMPO. Samples were taken before and after electrolysis and analyzed immediately in the EPR spectrometer.

Fig. 4 shows the typical spectra that were obtained during the DEPMPO experiments. In the sample taken before electrolysis, a small background signal is present that is likely due to degradation in the bottle. In the sample taken after electrolysis, a similar signal with a higher intensity is observed. The peaks match those of the simulated spectrum of •DEPMPO-OH and agrees with spectra of •DEPMPO-OH reported in literature [35,36]. Although the signal is rather weak, the known signature spectrum for •DEPMPO-OOH is not noticeable. A DFT study by Keith & Jacobs calculated that while the binding strength of •OOH is about twice as strong that of •OH on Pt surfaces, desorption of •OOH still takes place [37]. Other studies have postulated the •OOH intermediate as a possible soluble intermediate [8,9]. Therefore, the absence of the •OOH adduct implies that only •OH intermediates desorb during the ORR. This would mean that either no •OOH intermediate is formed, or that it reacts before it can desorb. We hope to investigate this matter further by increasing the charge consumed during the ORR, thus increasing the intensity of the EPR signal of any DEPMPO adducts. Hopefully, this will provide us with definite proof of the absence or presence of •DEPMPO-OOH.

![Fig. 3. Plot of the EPR intensity DI versus the charge Q for all nine electrodeposited electrodes. Circles, triangles, squares and diamonds represent the results after 0, 5, 10 and 15 min of electrolysis respectively. The dotted line is a linear fit of the results. Error bars are normal standard error, with \( N = 3 \).](image-url)
Conclusions

Using a combined electrochemical and ex situ EPR approach, we have shown that we can detect, identify and (semi)quantify free oxygen radicals produced by the ORR at porous electrodeposited Pt NPs. The size distribution and density of the particles does not appear to influence the trapping rate of oxygen radicals by DMPO within the studied NP distributions. Experiments with DEPMPO as a spin trap show that only ‘DEPMPO-OH is formed and no ‘DEPMPO-OOH is present. We show that our approach is a valid additional technique for investigating the reaction mechanism of the ORR from solution. We believe that our procedure allows for a more rigorous quantification of free radicals involved in electrochemical reactions and may provide future insights on the identification of soluble intermediates responsible for the degradation of electrocatalysts.

CRediT authorship contribution statement

Stephan den Hartog: Conceptualization, Methodology, Investigation, Writing - original draft. Mohammad Samanipour: Formal analysis, Writing - review & editing. H.Y. Vincent Ching: Conceptualization, Methodology, Writing - review & editing. Sabine Van Doorslaer: Conceptualization, Methodology, Writing - review & editing, Project administration, Funding acquisition. Tom Breugelmans: Supervision, Project administration, Funding acquisition. Annick Hubin: Writing - review & editing, Supervision, Project administration, Funding acquisition. Jon Ustarroz: Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2020.106878.

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Fig. 4. (a) EPR spectra taken immediately before (black) and after (magenta) 15 min of electrolysis in oxygenated 0.1 M HClO4 at 0.5 V vs. Ag/AgCl in presence of 10 mM DEPMPO. Simulations of ‘DEPMPO-OH (red) and ‘DEPMPO-OOH (blue) show that the signals in the experimental spectra belong to ‘DEPMPO-OH. See Table S2 of the Supporting Information for details of the EPR simulations. (b) Reaction pathways of DEPMPO with ‘OH and ‘OOH to the respective radical adducts.

• DEPMPO-OOH spontaneously degrades to ‘DMPO-OH with a half-life of approximately 20 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
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