



Short communication

The impact of dissolved reactive gases on platinum dissolution in acidic media

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ABSTRACT

Long-term stability of platinum catalysts still represents a massive challenge for applications in energy conversion devices like fuel cells. One of the key issues is platinum dissolution during potential perturbations in corrosive acidic environment. In order to improve the understanding on the complex dissolution processes at the electrode–electrolyte interface, we have thoroughly investigated polycrystalline platinum by utilizing online mass spectrometry in parallel to electrochemical experiments. In particular, the focus of the current study is the impact of dissolved, reactive gases on platinum dissolution in perchloric acid. While oxygen and hydrogen do not alter the behaviour compared to an electrolyte saturated with an inert gas, carbon monoxide introduces substantial alterations. Anodic dissolution during the oxide formation is suppressed in the case of CO bulk oxidation, however, upon the reduction of the surface in the negative going scan the amount of dissolved Pt is enhanced with a factor of three to four due to blockage of the reduced surface sites for re-deposition.

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1. Introduction

Due to the widespread use of platinum based materials in electrochemistry, an understanding of the interfacial processes is of high relevance for many applications. While various phenomena occurring at the Pt surface are fundamentally well studied, the dissolution of Pt during electrochemical experiments has received only little attention. Recently we have succeeded in coupling a micro-electrochemical scanning flow cell (SFC) with an inductively coupled plasma mass spectrometer (ICP-MS) that enables an unambiguous analysis of elements dissolved in the electrolyte with high sensitivity [1]. As a consequence the dissolution of electrode material can be directly monitored online by the SFC/ICP-MS as a function of the electrode potential or current density [2]. This technical advancement has in particular revealed that dissolution of Pt is a transient process, induced by both oxidation and reduction of the surface upon potential excursions above 1.1 V_{RHE}, while no steady-state dissolution occurs below potentials of significant oxygen evolution [2]. The “anodic” dissolution during positive potential sweeps is thereby depending on the interplay between exposure and passivation particularly of low-coordinated Pt on the surface during sub-surface oxidation that can be chemically dissolved. In contrast, the more severe “cathodic” dissolution during negative potential scans is determined by the amount of the formed oxides and the potential scan rate expressed by the competition between diffusion of ions away from the surface and their reduction/re-deposition [3].

While these findings obtained predominately under inert conditions, i.e. argon saturated electrolytes, are in principal representative for the dissolution processes at the Pt metal–liquid interface, additional effects due to dissolved and/or adsorbed reactive gases can play a role for applications under real operating conditions. Recently for instance Dubau et al. have demonstrated the variation of structural degradation mechanisms of Pt-based nano-particulated catalysts in the presence of several different gases [6]. Especially for electrochemical reactors like electrolyzers or fuel cells, where an extended triple-phase boundary region between gaseous, liquid and solid phase is established, such a fundamental understanding of the dependence of catalyst degradation and particularly Pt dissolution on the reactive gas can be crucial for the design of the catalyst material and electrode structure, as well as the optimization of operational conditions. Thus, in this work we utilize our unique experimental approach to investigate the impact of various gases dissolved in the electrolyte on the dissolution of polycrystalline platinum.

2. Experimental section

The measurements are performed using a micro-electrochemical scanning flow cell (SFC) directly connected to an inductively coupled plasma mass spectrometer (NexION 300×), so that the electrochemical and spectrometric signals are recorded in parallel. The coupled system was described in more detail in our previous studies [1,4]. The hardware components are controlled by an in-house programmed LabVIEW application [5] and the experimental results are presented on synchronized time scales. A polycrystalline platinum foil (99.99% MaTeCK) was used as a working electrode, and the contact area with the electrolyte was restricted to 1.1 mm². The counter electrode consisted of a thin

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graphite rod placed in the inlet tube, a Ag/AgCl reference electrode was situated in the downstream to prevent contaminations with chlorides [2]. All potentials are referred to the reversible hydrogen scale (RHE), determined independently on each measurement day. The solutions were freshly prepared from perchloric acid (Suprapur® Merck, <1 ppm Cl^- , i.e. for 0.1 M has less than ca. $0.4 \mu\text{M}$ of Cl^-) diluted with ultrapure water ($18.2 \text{ M}\Omega$, PureLab Plus system, Elga) and continuously purged during the experiments with argon, hydrogen, oxygen or carbon monoxide (Air Liquide, 5.0). All experiments were performed at room temperature (ca. $295 \text{ }^\circ\text{K}$). The electrode surface is electrochemically pre-treated before each experiment by potential cycling between 0.05 and $1.5 \text{ V}_{\text{RHE}}$ at a scan rate of 0.2 V s^{-1} .

3. Results and discussion

While our previous conclusions on platinum dissolution were predominantly based on the analysis of the interaction between the Pt surface and the electrolyte, the influence of the reactive gases like hydrogen, oxygen and carbon-monoxide on Pt dissolution was so far not considered. Taking into consideration that the adsorption of these gases can however be competitive with the adsorption of oxygen containing species originating from the solvent itself, and thus potentially interfere with processes at the surface of Pt like passivation, dissolution and/or surface reconstruction.

A comparison between the dissolution profiles in 0.1 M perchloric acid continuously saturated with one of the four different gases (Ar, H_2 , O_2 or CO) is presented in Fig. 1. The dissolution behaviour of Pt is practically identical for the oxygen, hydrogen and argon saturated solutions. For all three mentioned gases, dissolution appears in the anodic and cathodic branch of the voltammogram, where the cathodic one contributes significantly more to the overall dissolved amount of $6.9 \pm 0.3 \text{ ng cm}^{-2} \text{ cycle}^{-1}$ (up to $1.55 \text{ V}_{\text{RHE}}$) and $8.0 \pm 0.2 \text{ ng cm}^{-2} \text{ cycle}^{-1}$ (up to $1.65 \text{ V}_{\text{RHE}}$). Interestingly, the spectrometric response in the presence of carbon monoxide is quite different. In the positive potential scan, even after oxidation of the CO adlayer at around $0.85 \text{ V}_{\text{RHE}}$ and consequent bulk CO oxidation, the dissolution remains below the detection limit of ca. 10 ppt. This behaviour could be either a direct influence of dissolved CO on the

dissolution process during surface oxidation, or an indirect influence by restructuring of the surface during the preceding phase of CO adsorption.

A qualitatively different picture is observed during the negative potential sweep, which shows an enhancement in dissolution by a factor of three to four (25 and $36.6 \text{ ng cm}^{-2} \text{ cycle}^{-1}$) in comparison to the inert gas conditions as shown in Fig. 1. A more careful analysis of the dissolution profile reveals that the onset appears ca. 0.15 V more negative in comparison with the other three analysed gases. Having a clear notion that the process of Pt dissolution is strongly related with the process of platinum oxidation [3], we additionally monitored the influence of the overpotential for oxide formation in the CO saturated electrolyte, where the electrochemical signal is plotted in Fig. 2a. No dissolution is observed as long as the potential during the CV remains below ca. $1.1 \text{ V}_{\text{RHE}}$ (Fig. 2c). Once the potential window is extended above the potential for subsurface oxide formation, dissolution can be detected exclusively in the cathodic sweep, where the corresponding spectrometric signal is presented in Fig. 2b. An increase in the positive potential limit causes an increase in the amount of Pt dissolution, which can be related to the formation of more sub-surface oxides as in the case of inert gases. For all potential windows, the onset of the dissolution in the cathodic potential sweep is observed at ca. $0.85 \text{ V}_{\text{RHE}}$ in parallel with a decreasing oxidation current. At this potential CO strongly adsorbs on reduced Pt sites again and begins to block further bulk CO oxidation. It seems that in addition the adsorbed CO prevents the re-deposition of dissolved Pt-ions that leads to the observed enhanced dissolution signal compared to the other gases under similar conditions.

In order to shed more light on the impact of CO on Pt dissolution, we also followed an experimental protocol with dynamic gas exchange (Fig. 3). As shown already above, the amount of Pt dissolved during the CV in CO-saturated electrolyte is almost by a factor of four larger than during the initial CV in argon, while the anodic dissolution is suppressed. Interestingly, the first CV upon returning to argon purging again (at ca. 5500 s), which actually represents a CO-stripping experiment, induces less dissolution compared to the initial CV in argon (at ca. 200 s). The anodic dissolution is also suppressed in the CV at ca. 5500 s, where CO was initially still adsorbed on the surface. This suggests that the morphology and surface reorganisation induced

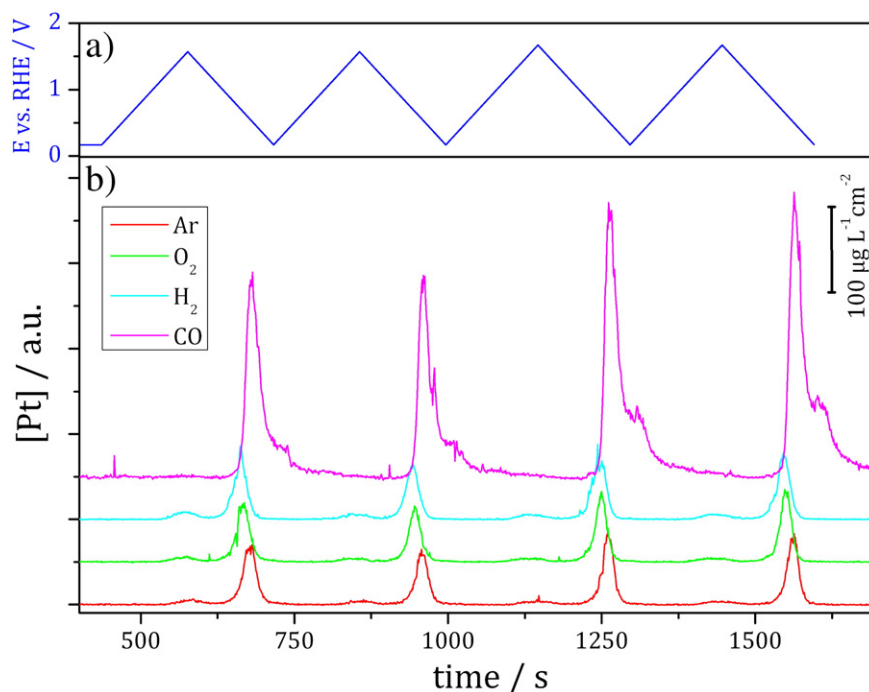


Fig. 1. a) Applied experimental sequence consisting of two cyclic voltammograms (CV) in the potential range from 0.1 up to 1.55 and from 0.1 up to $1.65 \text{ V}_{\text{RHE}}$ with a scan rate of 0.01 V s^{-1} ; b) The corresponding dissolution profiles in 0.1 M HClO_4 saturated and continuously purged with Ar, H_2 , O_2 or CO, all on the same time scale.

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