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Influence of the concentration of borohydride towards hydrogen production and escape for borohydride oxidation reaction on Pt and Au electrodes – experimental and modelling insights

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HIGHLIGHTS

- The borohydride oxidation reaction (BOR) was studied for Pt and Au electrode.
- The effect of the $NaBH_4$ concentration was studied.
- H_2 generation was measured by differential electrochemical mass spectrometry.
- A microkinetic model of the BOR was proposed.

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ABSTRACT

The Borohydride Oxidation Reaction (BOR), the anode reaction in a Direct borohydride fuel cell (DBFC), is complex and still poorly understood, which impedes the development and deployment of the DBFC technology. In particular, no practical electrocatalyst is capable to prevent gaseous hydrogen generation and escape from its anode upon operation, which lowers the fuel-efficiency of the DBFC and raises safety issues in operation. The nature of the anode electrocatalysts strongly influences the hydrogen escape characteristics of the DBFC, which demonstrates how important it is to isolate the BOR mechanism in conditions relevant to DBFC operation. In this paper, from a selected literature review and BOR experiments performed in differential electrochemical mass spectrometry (DEMS) in a wide range of $NaBH_4$ concentration (5–500 mM), a microkinetic model of the BOR for both Pt and Au surfaces is proposed; this model takes into account the hydrogen generation and escape.

1. Introduction

Fuel cells are high-energy-density competitors to batteries for mobile or portable application, their energy density not scaling to their power but instead to the size of their fuel tank and/or frequency of refueling. Proton exchange membrane fuel cells (PEMFC), the present standard, commercialized in all the fuel cell vehicles presently on the market, however suffer from practical limitations regarding the production, purification, transportation, compression and storage of their fuel (molecular hydrogen), which is particularly challenging for portable and mobile systems, but also from the high cost, low availability and insufficient durability of their Pt-based electrocatalysts [1,2]. Alkaline fuel cells (AFC), and in particular those fed directly with a liquid fuel (DLFAFC) could solve some of the issues that impede PEMFCs. The direct borohydride fuel cell (DBFC) is a special case of DLFAFC that presents very interesting

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potential, owing to the unique properties of its $NaBH_4$ fuel: $NaBH_4$ (i) is very easy and safe to store and transport as a powder or an alkaline solution, (ii) presents a high theoretical energy density, (iii) is (*a priori*) electrooxidized without generating strong surface poisons (contrary to CO poisoning during the electrooxidation of small organic molecules), and (iv) can be electrooxidized on many electrocatalysts, including noble [3–12] and non-noble [13–17] ones. The anodic borohydride oxidation reaction (BOR) theoretically generates 8 electrons, when complete. However, in practice, the BOR is in competition with non-Faradaic reactions (*e.g.* the BH_4^- heterogeneous hydrolysis) or with parasitic electrochemical reactions (*e.g.* the hydrogen evolution reaction, HER); both resulting in an undesirable generation of gaseous hydrogen. If this H_2 is not properly valorized at the anode, the fuel efficiency of the DBFC can severely drop, and safety issues may arise. So, one clearly needs to prevent (or at least minimize) the H_2 escape. This calls for adequate anode electrocatalysts and/or structures, but their rational design requires better understanding of the BOR mechanism.

Historically, studies dealing with DBFCs followed two distinct paths: on the one side, fundamental studies performed using electrochemical or spectroelectrochemical methods [6,18–29] and modeling [26,30–34] aimed to determine the BOR mechanism in model conditions (usually well-defined/simple noble electrocatalyst surfaces and dilute anolytes); on the other side, applied studies performed in close-to-real conditions (high-surface-area electrocatalysts integrated in thick electrodes, concentrated anolyte solutions) [35–48] aimed to reach high performances. An important variable, which differs between these “fundamental” and applied studies is the concentration of the borohydride anion. In most of the studies aiming to uncover the BOR mechanism, the BH_4^- concentration is on the order of (or smaller than) 10 mM, while a DBFC would practically operate at concentrations exceeding 100 mM (see *e.g.* Refs. [48,49]). There are numerous reasons for using low BH_4^- concentrations for fundamental studies, among them better reproducibility, cleaner conditions, observation of mass-transfer-limited BOR (which enables mass-transfer correction), smaller effect of ohmic drop, less hindrance of gas bubble formation (H_2 for instance) or of boron-oxides that can precipitate at the electrode surface [20,27,28]. All these advantages enabled the progressive determination of the BOR mechanism in “controlled model conditions” (*i.e.* for most of them at low concentrations) [6,18–34]. Unfortunately, these two approaches did progress rather independently from each other, and were not necessarily agreeing with one another in defining an optimized DBFC anode electrocatalyst. Indeed, the BOR being very complex (8 electrons exchanged in theory, structure sensitive, numerous intermediates, parallel (non)-faradaic reactions, *etc.*) the fundamental findings obtained in controlled environments (3-electrode cell, RDE setup, dilute electrolytes, *etc.*) are hardly transferable to practical DBFC application conditions. On the contrary, the DBFC system is affected by numerous, and sometimes uncontrolled, experimental variables, so that the rationalization of the performance for a given DBFC anode electrocatalyst is not an easy task [48,49]. For example, it has been generally demonstrated that hydrogen generation/escape upon BOR in a DBFC system is one of the main development hindrances encountered during the DBFC characterization, because H_2 production and escape in a direct liquid-fed fuel cell is unwanted, causing issues of energy efficiency, security, degradation, *etc.* [39,50–54]. While these DBFC studies demonstrated that the H_2 escape during operation is difficult to avoid, on Pt anodes it greatly depends on the experimental conditions (such as the anolyte flow rate, mass-loading of the Pt electrocatalyst per cm^2 of anode, BH_4^- concentration, presence of additives in the electrode or electrolyte), so that there is hope to at least reduce to a minimum (if not completely suppress) the H_2 generation while achieving good FC performance [39,42,55]. However, the variables ruling this generation of H_2 are not fully understood yet, and the discussions are often based on empirical findings in complex systems.

This study aims to go beyond these current limitations and to understand and model H_2 generation, oxidation and escape as a function of the borohydride fuel concentration. For that purpose, differential electrochemical mass spectrometry (DEMS) experiments were performed in a wide interval of BH_4^- concentrations relevant to the fuel cell operation (5, 50 and 500 mM) on sputtered porous layers of two of the most studied BOR electrocatalysts, platinum (Pt) and gold (Au), in order to monitor the extent of the H_2 escape upon BOR. Based on these experimental results, the BOR mechanism previously proposed for model Pt surfaces in dilute $NaBH_4$ solutions [26] was rectified and used for a mean-field microkinetic modelling in order to account for the effect of the increase of $[BH_4^-]$ on the escape of gaseous hydrogen for both Pt and Au surfaces. Then, the influence of the BH_4^- concentration on the BOR is discussed, bringing practical considerations for the development of the DBFC.

2. Experimental

The 1 M NaOH + 5, 50 or 500 mM $NaBH_4$ electrolytes were prepared according to the experimental procedures detailed in Ref. [26], using ultrapure water (18.2 MΩ cm, < 3 ppb total organic carbon water, MilliQ-gradient + Elix, Millipore®), monohydrated-NaOH crystals (99.99% purity, Merck Suprapur®) and $NaBH_4$ powder (98% purity, Merck).

A dedicated Pyrex®-based gastight spectro-electrochemical three-electrode cell was employed for the DEMS experiments, the design of which is inspired from Refs. [56–58]. This cell employs a glassy-carbon plate counter-electrode (CE), a freshly-prepared reversible hydrogen electrode (RHE) as reference electrode (RE) and a Pt (or Au) working electrode (WE, sputtered as a 50 nm-thick porous layer on a 20 μm-thick polytetrafluoroethylene (PTFE) porous sheet, with pores of 20 nm average diameter). The roughness factor of the sputtered electrodes is on the order of 10 cm^2 real per cm^2 geometric. The electrical connection of the Pt (or Au) WE is ensured by a Pt (or Au) wire (diameter 0.5 mm) ending by a Pt (or Au) ring; the connecting wire is inserted into the tube through which the Ar gas (5.0 Messer) is bubbled in the electrolyte solution, the tip of which is positioned at *ca.* 0.5 cm from the WE position, which enables (i) to avoid massive contact of this wire with the electrolyte (thus guarantying that the WE current mainly originates from the sputtered layer) and (ii) to agitate the electrolyte solution at the vicinity of the WE (thanks to the controlled bubbles flow – *ca.* 1 bubble per second). Finally, a rotator (Origatrode®, Origalys) with a PTFE shaft is positioned at the top of the cell to complete the mechanical stirring of the electrolyte in a laminar manner. As a result, although the WE is static, the convection of electrolyte is “controlled”, even though this control does not correspond to real “Levich conditions” as those encountered at a conventional RDE. The cell is mounted on a stainless-still frit onto which 2 bare PTFE membranes are positioned, just below the sputtered Pt (or Au) WE, this frit + PTFE membranes enabling the gas connection between the electrochemical compartment (above) and the vacuum compartment (below) for MS detection of the gaseous or volatile species. As high-concentration electrolyte solutions are used (up to 500 mM $NaBH_4$), leading to high currents at the WE, dynamic ohmic drop correction was applied in all electrochemical characterizations, using a computer-controlled SP300 potentiostat (Bio-Logic®). Finally, all the experiments were thermostated at $T = 25\,^{\circ}C$.

Prior to each experiment, the cell and glassware were soaked in concentrated Caro's acid (H_2SO_5) overnight and thoroughly rinsed with ultrapure water. For each experiment, the sputtered WE was

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