

Application-oriented investigation of amino acid poisoning at highly porous platinum electrodes for glucose oxidation

C. Köhler, L. Bleck, S. Kerzenmacher

Laboratory for MEMS Applications,
Department of Microsystems Engineering – IMTEK,
University of Freiburg,
Georges-Koehler-Allee 103, 79110 Freiburg, Germany

SUMMARY: We present a dedicated experimental procedure to systematically investigate the poisoning of platinum electrodes by physiological amino acids. In contrast to previous studies on smooth surfaces [4,5], we employ highly porous platinum electrodes of applicational relevance for implantable glucose fuel cells and potentially also sensors. First results show that also at highly porous platinum electrodes the amino acids histidine and glycine lead to significant electrode poisoning, as expected from previous studies on smooth electrodes [4,5]. In contrast to literature, the sulfur-containing AAs methionine and cysteine do not significantly affect the performance of highly porous electrodes under typical fuel cell operation conditions. For the development of poisoning-resistant electrodes for application with implantable glucose fuel cells and sensors it is thus highly relevant to study the poisoning effect of all physiological AAs.

INTRODUCTION: Highly porous platinum electrodes are of great interest for the use in implantable glucose fuel cells or sensors [1,2]. In this context, the main challenge is electrode poisoning resulting from the adsorption of amino acids (AAs) present in body fluids. To systematically develop poisoning-resistant electrodes it is essential to know the adsorption behavior of AAs at highly porous platinum surfaces. In previous studies different amino acids have already been distinguished by their poisoning effect, which has been related to their functional groups [3-5]. However, so far no comprehensive study including all physiological AAs has been reported. Furthermore previous studies considered mostly smooth platinum electrodes with a low specific surface area, which are of little relevance for practical application.

EXPERIMENTAL PROCEDURE: Porous platinum electrodes were fabricated by repeated pulsed electrodeposition of PtCu alloy and the selective removal of the non-noble copper (9 s @ -0.5V and 4.5 s @ 0.7 V vs. SCE, in total 1200 pulses in an acidic electrolyte containing 20 mmol Pt⁴⁺ and Cu²⁺), similar to the method presented in [6]. The roughness factor of the electrodes amounted to 6800 ± 700 . The experimental procedure to characterize AA poisoning consists of a sequence of cyclic voltammetry and continuous galvanostatic load experiments. The procedure is divided into four blocks:

- (1) Cleaning of the electrode by cyclic voltammetry between -0.9 and 1.2 V vs. SCE
- (2) Continuous galvanostatic load at $10 \mu\text{A cm}^{-2}$ (typical current density of implantable glucose fuel cells) in the presence of AAs to induce poisoning
- (3) Continuous galvanostatic load at $10 \mu\text{A cm}^{-2}$ in the absence of AAs to induce desorption and characterize the reversibility of AA adsorption
- (4) A final cyclic voltammetry experiment as above to clean the electrode

All experiments were performed in de-aerated phosphate buffered saline solution at 37°C, containing 3 mmol glucose and the individual AAs at physiological concentration.

RESULTS AND DISCUSSION: The first results using five selected AAs with different functional groups and characteristics under fuel cell relevant operation conditions are shown in Fig. 1. As can be seen, the presence of histidine and glycine leads to pronounced electrode poisoning, similar to previous results obtained with smooth electrodes [4,5]. An unexpected result was found for the sulfur-containing amino acids (methionine and cysteine), which in contrast to studies at smooth electrodes showed no significant poisoning. This may be related to the high specific surface of the investigated electrodes, which despite partial coverage by adsorbed methionine and cysteine offers sufficient reaction sites for glucose oxidation. Our preliminary investigations also showed that AAs with the same functional group, e.g. leucine and glycine can exhibit a significant difference in the degree of poisoning. This indicates that not only the functional group of the AA, but also other characteristics such as hydrophobicity, charge, or molecule size play an important role in catalyst poisoning. No significant recovery of performance was observed when the electrodes were first exposed to AAs and subsequently operated in AA-free buffer. This indicates irreversible adsorption to the platinum surface for the investigated five AAs.

CONCLUSION AND OUTLOOK: We present for the first time a dedicated experimental approach to characterize the poisoning behavior of highly porous platinum electrodes by amino acids under operation conditions relevant for implantable glucose fuel cells. First results indicate that previous studies performed with smooth electrodes are not fully transferable to highly porous electrodes relevant for practical applications. In future, we will therefore expand our studies to quantify the poisoning behavior of all physiological AAs. These results will be highly relevant for the development of poisoning-resistant electrodes for implantable glucose fuel cells and possibly also sensors.

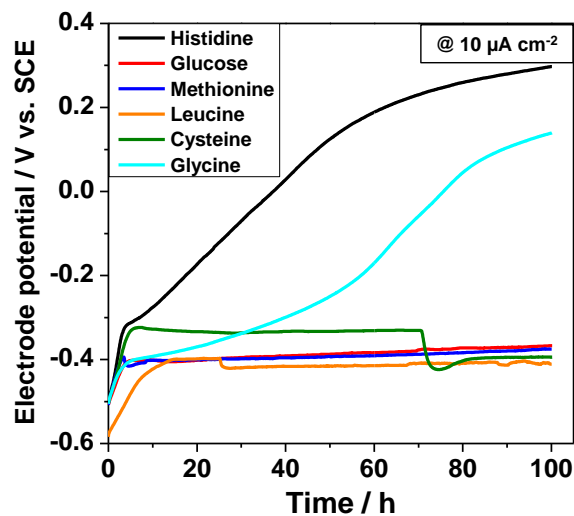


Figure 1: Continuous galvanostatic load experiments @ $10 \mu\text{A cm}^{-2}$ in PBS + glucose with addition of different amino acids.

- [1] Kerzenmacher et al., *JOPS*, **182** (2008), 1-17.
- [2] Yuan et al., *Adv. Funct. Mat.*, **15** (2005), 803-809
- [3] Rao et al., *Biomat. Med. Dev. and Artif. Org.*, **6** (1978) 127-149.
- [4] Giner et al., *J. Echem. Soc.*, **128** (1981) 2106-2114.
- [5] Hibbert et al., *J. Echem. Soc.*, **148** (2001) E1-E7.
- [6] Kloke et al., *Adv. Mat.*, **24** (2012), 2916-2921.