



PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9

Title: PHYSICAL CHEMISTRY 2014 (Proceedings)

Editors: Ž. Čupić and S. Anić

Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia

Publisher: Society of Physical Chemists of Serbia

For Publisher: S. Anić, President of Society of Physical Chemists of Serbia

Printed by: “Jovan” Printing and Publishing Company; 200 Copies;

Number of pages: 6+ 441; **Format:** B5; Printing finished in September 2014.

Text and Layout: “Jovan”

Neither this book nor any part may be reproduced or transmitted in any form or by any means, including photocopying, or by any information storage and retrieval system, without permission in writing from the publisher.

200 - *Coppy printing*

PHYSICAL CHEMISTRY 2014

*12th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Organized by
The Society of Physical Chemists of
Serbia*

*in co-operation
with_*

Institute of Catalysis Bulgarian Academy of Sciences

*Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy
of Sciences*

Faculty of Physical Chemistry, University of Belgrade, Serbia

*Institute of Chemistry Technology and Metallurgy,
University of Belgrade, Serbia*

Vinča Institute, University of Belgrade, Serbia

Institute of General and Physical Chemistry, Serbia

Faculty of Pharmacy, University of Belgrade, Serbia

International Organizing Committee

Chairman: S. Anić (Serbia)
Vice-chairman: M. Gabrovska (Bulgaria)
V. A. Sadykov (Russia)

Members:

N. Cyjetičanin (Serbia), S. N. Blagojević (Serbia), M. Daković (Serbia), T. Grozdić (Serbia), D. Jovanović (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), J. Marković-Dimitrić (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Ostrovski (Serbia), I. Pašti (Serbia), M. Petković (Serbia), A. Popović-Bjelić (Serbia), B. Simonović (Serbia), D. Stanisavljev (Serbia), B. Šljukić (Serbia), N. Vukelić (Serbia), V. Vukojević (Sweden)

International Scientific Committee

Chairman: Ž. Čupić (Serbia)
Vice-chairmans: V. N. Parmon (Russia)
S. Rakovsky (Bulgaria)

Members:

B. Adnađević (Serbia), S. Anić (Serbia), A. Antić-Jovanović (Serbia), G. Bačić (Serbia), A. Kellarakis (Greece), R. Cervellati (Italy), V. Dondur (Serbia), Ivan Gutman (Serbia), S. D. Furrow (USA), K. Hedrih (Serbia), M. Jeremić (Serbia), A. V. Knyazev (Russia), Lj. Kolar-Anić (Serbia), V. Kuntić (Serbia), Z. Marković (Serbia), S. Mentus (Serbia), Š. Miljanić (Serbia), M. Perić (Serbia), M. Plavšić (Serbia), D. M. F. Santos (Portugal), G. Schmitz (Belgium), I. Schreiber (Czech), P. Sevčík (Slovakia), B. C. Simionescu (Romania), N. Stepanov (Russia), D. Todorović (Serbia), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia)

Local Executive Committee

Chairman: S. Blagojević
Vice-chairmans: A. Ivanović-Šašić

Members:

P. Banković, N. Bošnjaković, J. Dostanić, A. Đerić, A. Ignjatović, A. Jović, N. Jović-Jovičić, D. Lončarević, J. Krstić, J. Maksimović, V. Marković, M. Milenković, S. Maćešić, V. Marković, B. Nedić, N. Potkonjak, D. Ranković, M. Stević, M. Žunić, M. Ristić,

THE INFLUENCE OF NAFION ON OXIDATION OF GLUCOSE ON GOLD ELECTRODE FROM ALKALINE SOLUTIONS

T. Mudrinić, Z. Mojović and A. Ivanović-Šašić

*University of Belgrade, Institute of Chemistry, Technology and Metallurgy,
Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000
Belgrade, Republic of Serbia*

ABSTRACT

The influence of Nafion on oxidation of glucose on gold electrode in 0.1 M NaOH solution was investigated. The presence of Nafion on the surface of gold electrode decreased the rate of glucose oxidation in alkaline solution. The mechanism of glucose oxidation is not changed by the presence of Nafion.

INTRODUCTION

The electrooxidation of sugars, particularly glucose, was investigated for applications in glucose sensors as well as fuel cells for cardiac pacemakers. The enzyme-based glucose sensors are developed and thoroughly investigated and so far showed good sensitivity and selectivity. However, major drawback of enzyme-based glucose sensors is their lack of stability of enzymes. For this reason the investigation on non-enzymatic glucose sensors raised a great interest. The practical application of non-enzymatic sensors is hindered by their lack of selectivity and fouling of the electrode [1]. The gold electrode showed good electrocatalytic activity for glucose oxidation in neutral and alkaline electrolytes. The gold electrode also shows high sensitivity toward chloride ions in neutral solutions [2], what makes this electrode inadequate for application under physiological conditions. The modification of gold electrode by different metal ad-layers showed some improvement [3]. Nafion (perfluorinated sulphonate ionomer) has negative charge, so foreign species such as ascorbic acid, paracetamol, uric acid, etc. are readily repelled [4]. The aim of this paper was to investigate influence of Nafion on glucose oxidation on gold electrode in alkaline solution.

EXPERIMENTAL

Glucose oxidation on gold electrode was investigated in a 0.1 M NaOH in a three-electrode glass cell with Ag/AgCl (sat'd) as a reference electrode,

while a platinum foil served as a counter electrode. The influence of Nafion was investigated on Nafion covered gold electrode. The droplet of solution of Nafion (5 wt. %) was placed on the gold electrode. After evaporation of solvent Nafion film was formed on the electrode surface. Device used for the electrochemical measurements was a 757 VA Computrace Metrohm.

RESULTS AND DISCUSSION

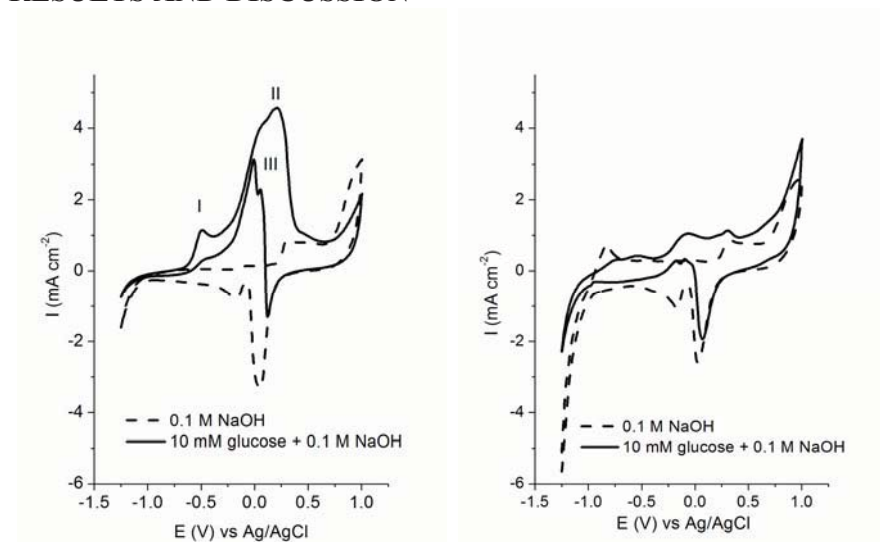


Figure 1. Voltammograms of bare gold electrode (left) and Nafion covered gold electrode (right) in 0.1 M NaOH without (dashed) and with 10 mM glucose (solid).

The cyclic voltammograms of Au electrode in 0.1M NaOH (Fig.1) show peaks of gold oxide formation and reduction at 0.30 and 0.05 V, respectively. The cyclic voltammogram recorded in the presence of glucose is presented at the same figure. The anodic peak at -0.6 V is followed by broad peak at approximately 0 V. The peak at -0.6 V is ascribed to the formation and adsorption of intermediate compounds, while the other peak represents the direct oxidation of glucose in the anodic direction (II). This peak has a large left shoulder indicating the occurrence of several reactions [5]. The cathodic peak on the negatively going sweep corresponds to direct oxidation of glucose in cathodic direction. The direct oxidation of glucose occurs after the oxides are removed from the surface of the electrode. The AuOH sites are considered to be the active species for glucose oxidation. Therefore, the rate of glucose oxidation depends on the number of AuOH sites. The oxidation of glucose starts with the formation of AuOH, and

proceeds until gold oxide is formed at sufficiently high positive potentials and the current of glucose oxidation decreases. In negative going sweep the catalytic oxidation of glucose starts again as soon as gold oxide is reduced and AuOH sites are formed again.

Cyclic voltammograms at different scan rates were recorded in order to investigate the kinetics of glucose oxidation. Plotting $\log i$ vs. $\log v$ shows that peak II is controlled by diffusion (slope close to 0.5). However, the same plot for peak I shows two slopes. At higher scan rates (150 - 500 mVs^{-1}) the slope is close to 0.5 indicating diffusion controlled process. However, at lower scan rates (10 - 100 mVs^{-1}) the obtained slope amounts 0.17 indicating a mechanism with numerous adsorbed species and products formed [6]. The current density of re-oxidation peak III decreases and the peak position shifts toward negative direction with increased scan rates, which indicates the poisoning of the electrode surface [7]. The potentials of peaks I and II are proportional to the logarithm of scan rate. From the slope of the E_p vs. $\log v$ curve, the Tafel slope can be obtained. The obtained Tafel slopes amount 50 and 56 V dec^{-1} for peaks I and II, respectively, what indicates that a two-electron transfer process is the rate limiting step for these reaction. The current function ($ip/v^{1/2}$) of peak I decreases with v , which is characteristic of a coupled chemical reaction following the electron transfer (EC mechanism) [8]. This type of mechanism occurs quite frequently in organic compounds which undergo electrochemical oxidation or reduction and produce a reaction species (radical or radical ions) that tend to dimerize. The current function of peak II shows slower decline indicating that process is not free from kinetic complications.

The cyclic voltammogram of Nafion covered gold electrode (Au/Nafion) exhibited additional anodic peak in comparison to CV of bare gold electrode (Fig. 1). This peak appeared in the potential region of hydrogen desorption. Upon successive addition of increasing amounts of glucose this peak started to diminish followed by the appearance of new peak at somewhat higher potentials. This peak might be associated to the adsorption and partial oxidation of glucose. The oxidation of glucose and formed gluconolactone at higher potential are clearly separated, although the obtained currents are about five times lower than currents obtained on bare gold electrode. At the reverse sweep the peak of reduction of gold oxide gradually decrease and two separated peaks of oxidation of glucose/glucose products appeared.

Plotting $\log i$ vs. $\log v$ shows that peak II is controlled by diffusion (slope close to 0.5). As in the case of bare gold electrode, this plot for peak I showed two slopes. At higher scan rates (150 - 500 mVs^{-1}) the slope is close to 0.8 indicating mixed controlled process. At lower scan rates (10 - 100 mVs^{-1}) the obtained slope amounts 0.3 what suggests a mechanism with

numerous adsorbed species and products formed. The current function ($i_p/v^{1/2}$) of both peaks decreases with v which is characteristic of a coupled chemical reaction following the electron transfer (EC mechanism).

CONCLUSIONS

The influence of Nafion on oxidation of glucose on gold electrode in alkaline solution was investigated. The presence of Nafion on the surface of gold electrode lead to decrease of the rate of glucose oxidation in alkaline solution. The decrease of reaction rate is consequence of reduced concentration of glucose and OH ions at the electrode surface. It seems that the mechanism of glucose oxidation is not changed by the presence of Nafion.

ACKNOWLEDGMENT

This work was supported by the Ministry of Education, Science and Technological Development of Republic Serbia (contract No III 45001).

REFERENCES

- [1] K.E. Tonghill, R.G. Compton, *Int. J. Electrochem. Sci.*, 2010, 5, 1246-1301.
- [2] Z.B. Vassilyev, O.A. Khazova, N.N. Nikolaeva, *J. Electroanal. Chem.*, 1985, 196, 127-144.
- [3] S.B. Aoun, Y. Dursun, T. Koga, G.S. Bang, T. Sotomura, I. Taniguchi, *J. Electroanal. Chem.*, 2004, 567, 175–183.
- [4] H. Liu, J. Deng, *Electrochim. Acta*, 1995, 40, 1845–1849.
- [5] M. Tominaga, T. Shimazoe, M. Nagashima, I. Taniguchi, *Electrochem. Commun.*, 2005, 7, 189–193.
- [6] P. Parpot, P.R.B. Santos, A.P. Bettencourt, *J. Electroanal. Chem.*, 2007, 610, 154–162.
- [7] A. Liu, E. Liu, G. Yang, N. Win Khun, W. Ma, *Pure Appl. Chem.*, 2010, 82, 2217-2229
- [8] A. Bard, L. Faulkner, *Electrochemical Methods Fundamental and Applications*, Wiley, Chichester 1980.