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Electrochemical Reduction of Xylose

Spasojevic, M., Lidija Rafailovic, Lenka Ribic-Zelenovic
Faculty of Agronomy, Cacak, Serbia and Montenegro

Abstract: By electrolysis of the solution of xylose and potassium- bromide in the cell with the cationic selective membrane, xylitol and xylonic acid were obtained simultaneously. On the active titanium anodes RuO_2 / TiO_2 the evolved bromine at low overvoltage hydrolyse into hypobromite which oxidizes xylose to δ – xylolactone, which then by the spontaneous conversion turns into xylonic acid. By the electrolysis of the solution on the cathode apart from the wanted reaction of the reduction of xylose to xylitol, the parallel reaction of the evolution of hydrogen happens.

The amalgamated zinc as the cathode was employed considering the reaction of hydrogen evolution on that cathode take place at high overvoltage. By the suitable selection of the parameters of electrolysis from the sulphate bath the layer of zinc with the wanted characteristics was deposited on the copper net. The amalgamated zinc of the suitable concentration was formed by dipping the layer in the solution of $HgCl_2$ for a certain period of time. Experimentally it was found out that the cathodic current efficiency of xylitol depends on the current density, concentration of xylose and the temperature of the solution. By the electrolysis of the solution of xylose the concentration $C>0,8M$ at $t>40°C$, in the range of the current density of electricity 100 $mA/cm^2<j<400$ mA/cm^2, on the amalgamated zinc cathode xylitol is obtained with the high current efficiency $\eta>90\%$. The obtained experimental data show that the zinc amalgamated cathode with the good mechanical and electrochemical characteristics may be used in the industrial cells for producing xylitol.

Key words: xylose, xylonic acid, xylitol, catalyst, selective membrane, amalgamated zinc cathode.

Introduction

Xylitol is one of the mass-produced products of the pharmaceutical industry. It is used as a sweetener accepted by medical science and recommended for people suffering from diabetes. Xylitol is used for syrup production, also. Xylonic acid and

xylonates are powerful polydentate ligands. They easily form helate complexes and are therefore used for the washing agent production.

Xylose is a relatively cheap substance obtained by hydrolysis from beech tree waste, straw and other waste materials. Industrial xylitol production, based on the catalytic hydrogenation of xylose, is performed at high pressures (about 8 10^5 Pa) and at high temperatures (about 350 K) with high energy consumption. There is also high energy consumption in the process of the electrolytic production of hydrogen used for the xylose hydrogenation. High energy consumption in the xylitol production has caused intensive investigations aimed at development of new and more economical method of its obtainment (Pork, et al., 1985; Cantor, et al., 1990;.Jokic, et al., 1988, 1991, 1991; Cvijovic, et al., 1998).

A new electrochemical method for the simultaneous production of xylitol and xylonic acid from xylose has been developed over the past few years (Pork, et al., 1985; Cantor, et al., 1990;.Jokic, et al., 1988, 1991, 1991). The electrochemical cell contains graphite anodes and amalgamated zinc cathodes. However, the amalgamated zinc cathodes have bad mechanical characteristics.

The aim of this paper was to develop new cathodes for the reaction of the reduction of xylose with good mechanical characteristics, of high selectivity and catalytic activity.

Experimental

The cell with the cationic selective membrane was used for the electrochemical investigations of the simultaneous xylose reduction and oxidation (Flemion, Asahi Glass). The anode was active titanium electrode 40 mol.% RuO_2, 60 mol.% TiO_2 of 10 cm^2 surface area. The cathode used in the process was obtained by the electrochemical deposition of zinc from the sulfate bath (35.0 g/dm^3 $ZnSO_4$, 30.0 g/dm^3 $(NH_4)_2SO_4$ at t = 22°C. First, a shiny compact adherent zinc layer was formed on the copper net at a low current density of 5.0 $mAcm^{-2}$. Then, the current density was increased to 20.0 $mAcm^{-2}$ at which a rough slightly spongy zinc layer of great actual surface area was deposited. The amalgamated cathode was obtained by dipping the layer in the solution of 0.1 M $HgCl_2$ for 60 s at t = 20°C.

The basic electrolyte for the electrochemical investigations was 0.8 M KBr. The concentration of xylose ranged from 0.4 to 1.0 M. The experiments were conducted at the pH of the solution of 8.0 and at temperatures ranging from 20-80°C. All the solutions were obtained from triple-distilled water and Merck chemicals. The cathodic current efficiency was determined by measuring the rate of hydrogen evolution. A graduated burette was placed above the cathode. The period of time needed for filling the burette of specific volume with the cathode-evolved hydrogen was measured.

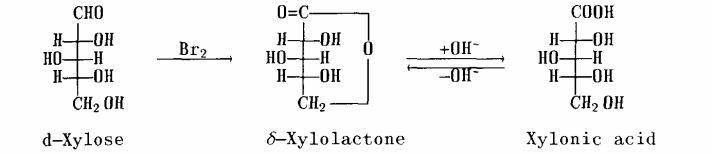
Results and Discussion

On the titanium anodes activated by solid solutions of rutile structure RuO_2 / TiO_2 elementary bromine evolves at low overvoltage and hydrolyzes in neutral and alkaline environments into hypobromite and hypobromite acid:

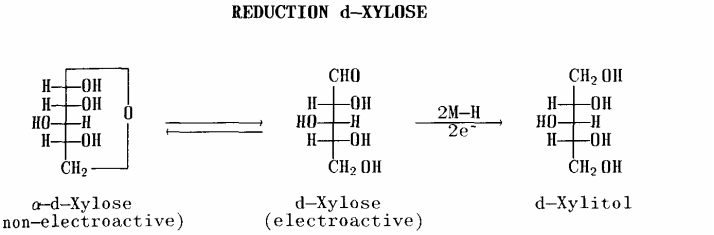
The obtained hypobromite and hypobromite acid (active bromine) oxidizes D – xylose to δ-xylolactone which then by spontaneous conversion turns into xylonic acid (reaction 3).

$$2Br^- \rightarrow Br_2 + 2\,e \quad (1)$$

$$Br_2 + H_2O \rightarrow HBrO + H^+ + Br^- \quad (2)$$



(3)



(4)

Scheme 1. Cathodic and anodic pathways of α - D- xylose oxidation and reduction, respectively

The anodic current efficiency is about 97%. Losses occur due to the oxidation of active bromine (Jokic, et al.,1991; Cvijovic, et al., 1998). The cationic selective membrane prevents the transport of active bromine and δ-xylolactone to the cathode surface and thus their reduction. The yield of xylonic acid calculated on the xylose consumption in the anolyte is 100% .

By the electrolysis of the solution 0.8 M KBr + x M $C_5H_{10}O_5$ on the cathode, apart from the wanted reaction of the reduction of D-xylose to xylitole (reaction 4), the reaction of the reduction of D-xylosis to 1-deoxypentite and that of D-lyxose to 2-deoxypentite as well as the reaction of the evolution of hydrogen (reactions 5, 6, 7) occur. D-lyxose is obtained by the isomerization of D-xylose. In the pH solution range of 6.0 to 9.0, the reaction of isomerization and those of the reduction of D-lyxose and D-xylose to deoxypentite do not practically happen. In this pH range, the cathodic current losses are caused only by the reaction of the evolution of hydrogen. Balance between cyclic hemiacetal and oxycarboniylic form of xylose is established in the solution. By mutarotation one form transform into another. Only the aldehyde xylose form reacts on the cathode (Pork, et al., 1985; Cantor, et al., 1990;.Jokic, et al., 1988, 1991, 1991; Cvijovic, et al., 1998).

$$H^+ + e \rightarrow H_{ad} \quad (5)$$

$$H^+ + e + H_{ad} \rightarrow H_2 \quad (6)$$

$$H_{ad} + H_{ad} \rightarrow H_2 \quad (7)$$

Amalgamated zinc was used as the cathode due to high overvoltage of the reaction of the evolution of hydrogen. The composition of amalgam was determined in such a way as to control the reactions (6) and (7) to the maximum favoring the reaction between the adsorbed hydrogen atoms and adsorbed molecules of the oxycarbonylic form of D-xylose. The content of mercury in the amalgam was determined by the period of time of holding the zincate electrode in the $HgCl_2$ solution. The optimal cementation time was 60 s.

Figure 1 presents the dependence of the cathodic current efficiency of xylitol on the current density and solution temperature. At the solution temperature of t=20°C, with the increase of the current density, the cathodic current efficiency continually decreases. At t=20°C, with the increase of the current density, the evolution of hydrogen occurs more rapidly than the reaction of the xylose reduction.

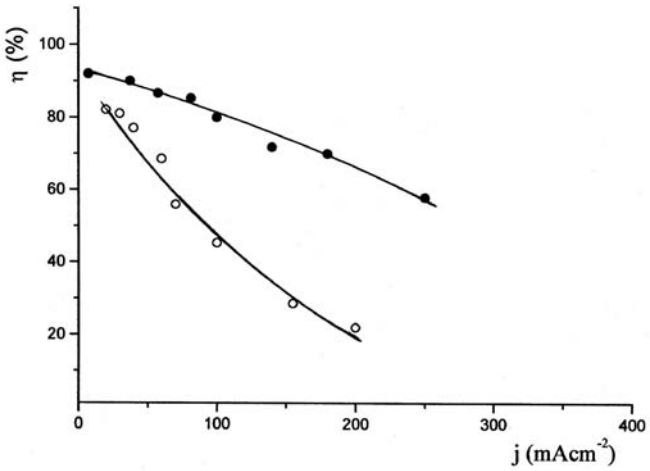


Figure 1 – Cathodic current efficiency of xylitol plotted as a function of current density for various temperature of the solutions: • - 1.0M $C_5H_{10}O_5$; o - 0.4 M $C_5H_{10}O_5$

At temperatures higher than 20°C, with the increase of the current density, the current efficiency first increases up to the maximum value and then decreases with the further increase of the current density.

At low current densities, the current efficiency decreases with the increase of the solution temperature. However, at high current densities, the current efficiency increases with the increase of temperature. At medium current densities, with the solution temperature increase, the current efficiency first increases reaching maximum value and then decreases (Figure 2).

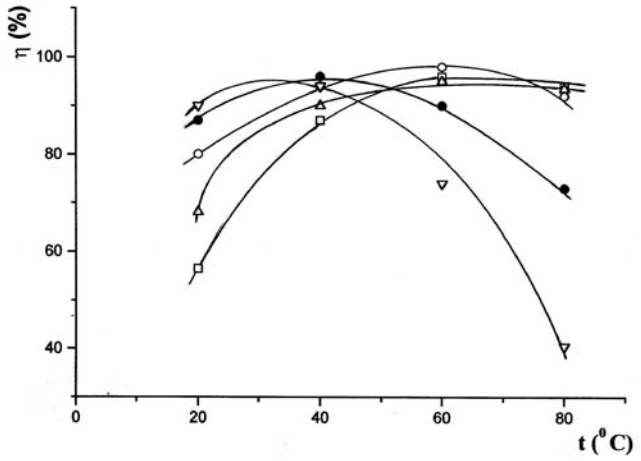


Figure 2 – Cathodic current efficiency of xylitol plotted as a function of temperature of the solution for various current densities: □ - 250 mAcm^{-2}; Δ - 180 mAcm^{-2}; o - 100 mAcm^{-2}; • - 60 mAcm^{-2}; ∇ - 40 mAcm^{-2} (1.0M $C_5H_{10}O_5$, 0.8M KBr)

Figure 3 presents the effect of the current density and concentration of xylose on the cathodic current efficiency of xylitol. With the increase of the concentration of the solution, the current efficiency also increases. The increase was more obvious at higher current densities.

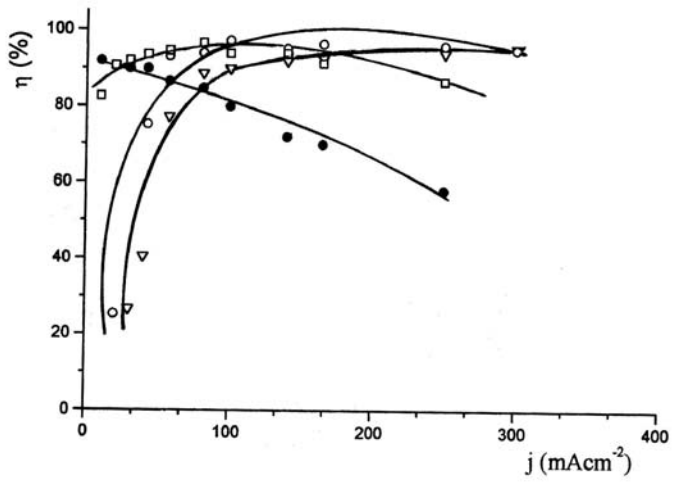


Figure 3 – Cathodic current efficiency of xylitol plotted as a function of current density for various D-xyloze concentrations: ∇ - 80°C; o - 60°C; □ - 40°C; • - 20°C; (1.0M $C_5H_{10}O_5$, 0.8M KBr).

The presented experimental results show that by the electrolysis of the solution of xylose, the concentration C>0.8 M at temperatures higher than 40°C, high current efficiency of xylitol η>90% can be obtained at high current densities 100 $mAcm^{-2}$ < j < 400 $mAcm^{-2}$. This indicates that the cathode with good mechanical characteristics, made of zinc amalgam formed on the copper net, may be successfully used in the industrial cells for producing xylitol by the electrolysis of the xylose solution.

Conclusion

The process of obtaining the amalgamated zinc cathode for the electrochemical cells for simultaneous production of xylitol and xylonic acid by the electrolysis of the xylose solution has been developed. The layer of zinc is obtained by electrodeposition from sulfate solutions on the copper net. The amalgamated zinc of the suitable concentration is formed by dipping the layer in the solution of $HgCl_2$ for a certain period of time. The obtained cathode has good mechanical characteristics.

The dependence of the cathodic current efficiency on the current density, xylose concentration and solution temperature has been experimentally established. On the basis of the stated dependence, optimal conditions for the electrochemical production of xylitol may be determined. By the electrolysis of the solution of xylose concentration C > 0.8M, at t>40°C, at high current densities of 100 $mAcm^{-2}$ < j < 400 $mAcm^{-2}$, on the amalgamated zinc cathode, xylitol is obtained with the high current efficiency η>90%.

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ELEKTROHEMIJSKA REDUKCIJA KSILOZE

- originalni naučni rad -

Spasojevic, M., Lidija Rafailovic, Lenka Ribic-Zelenovic
Agronomski fakultet, Čačak

Rezime

Elektrolizom rastvora ksiloze i kalijumbromida u ćeliji sa katjonselektivnom membranom simultano je dobijen ksilitol i ksilonska kiselina. Na aktivnim titanskim anodama RuO_2 / TiO_2 izdvojeni brom na malim prenapetostima hidrolizuje, dajući hipobromit koji oksiduje ksilozu do δ-ksilolaktona, koji potom spontanom konverzijom prelazi u ksilonsku kiselinu. Elektrolizom rastvora ksiloze na katodi se pored željene reakcije redukcije ksiloze do ksilitola odvija i paralelna reakcija izdvajanja vodonika.

U ovom radu kao katoda korišćen je amalgam cinka zbog velike prenapetosti reakcije izdvajanja vodonika. Podesnim izborom parametara elektrolize iz sulfatnog kupatila na bakarnoj mreži istaložena je prevlaka od cinka željenih karakteristika. Amalgam cinka podesne koncentracije formiran je zamakanjem prevlake određeno vreme u rastvor $HgCl_2$. Dobijena elektroda imala je dobra mehanička svojstva.

Eksperimentalno je ustanovljena zavisnost katodnog iskorišćenja struje po ksilitolu od gustine struje, koncentracije ksiloze i temperature rastvora. Elektrolizom rastvora ksiloze koncentracija $C > 0{,}8M$, na $t > 40°C$, u oblasti gustina struje od $100\ mAcm^{-2} < j < 400\ mAcm^{-2}$, na cinkamalgamskoj katodi dobijen je ksilitol sa velikim iskorišćenjem struje $\eta > 90\%$. Dobijeni eksperimentalni podaci su pokazali da se cinkamalgamska katoda dobrih mehaničkih i elektrohemijskih svojstava može primeniti u industrijskim ćelijama za proizvodnju ksilitola.