

The Kinetics of the Electrochemical Reduction of Xylose on Amalgamated Zinc

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Abstract: During the electrolysis of an aqueous solution of xylose, two parallel reactions take place on the cathode i.e. the reduction of xylose to xylitol and hydrogen evolution.

To favour the desired reaction of xylose reduction, amalgamated zinc is used to perform the reduction in this study. The catalytic amalgamated coating is formed by the electrodeposition of a zinc coating having desired properties on a copper mesh from a sulfate bath and its subsequent immersion into the HgCl_2 solution to obtain the amalgamated zinc of adequate concentration.

The present study focuses on the kinetics and mechanism of two parallel reactions of hydrogen evolution and xylose reduction on amalgamated zinc from a solution containing xylose and Na_2SO_4 as a basic electrolyte. The hydrogen evolution reaction occurs through two parallel mechanisms, either in the presence or absence of xylose. At lower overpotentials, hydrogen is evolved on zinc oxide in three consecutive elementary steps. The overall rate of the hydrogen evolution reaction within the limiting current range is governed by the heterogeneous chemical step involving a Zn-H species. At potentials more negative than -2.0 V, the reaction takes place on the metal surface through the Volmer-Heyrovsky mechanism.

Xylose is adsorbed on the metallic zinc. At potentials more negative than -1.25 V, the adsorbed xylose molecules are reduced with Zn-H to xylitol. The cathodic polarization curves, in either the presence or absence of xylose, were used to determine the cathodic current efficiency for xylitol production, which is in good agreement with the values obtained by other methods.

Key words: xylose, xylitol, amalgamated zinc cathode, electrolysis

Introduction

Xylitol is used for syrup production in food industry and as a non-caloric sweetener in human diet, particularly for people suffering from diabetes.

The conventional industrial process of xylitol production requires catalytic hydrogenation of xylose. Xylose is a relatively inexpensive substance. It originates from hydrolysis of biomass waste. However, catalytic xylose hydrogenation takes place at high pressures, high temperatures and at a high energy consumption rate. The high energy consumption rate has induced intensive studies aimed at developing new and more cost-effective routes of xylitol production. The studies have resulted in the development of a new procedure for the simultaneous production of xylitol and xylonic acid by electrolysis of an aqueous solution of xylose (Pork *et al.* 1985, Cantor and Peniston 1990, Jokić *et al.* 1988, 1989, 1991, Spasojević *et al.* 2003).

During the electrolysis of the xylose solution, two parallel reactions occur on the cathode i.e. the reduction of xylose to xylitol and hydrogen evolution. An amalgamated zinc cathode is used for xylitol production in the electrolyzer in order to favour the desired xylose reduction reaction, due to a high overpotential for hydrogen evolution. The amalgamated zinc electrode has poor mechanical properties.

The objective of this study was to develop a new type of amalgamated zinc electrode and examine its catalytic and selective characteristics. The mechanism of xylose reduction and hydrogen evolution reactions was investigated. A thorough knowledge of the mechanism of these reactions enables modelling of the composition and structure of the cathode material.

Experimental

A standard electrochemical cell was used in the experiment. The anode used was a dimensionally stable anode (DSA) of 10 cm². The cathode was obtained by electrochemical deposition of zinc from a sulfate bath (35.0 g/dm³ ZnSO₄; 30.0 g/dm³ (NH₄)₂SO₄) at t=25°C. A compact adherent zinc coating was formed on a copper substrate at a low current density of 5.0 mA cm⁻². Then, a rough coating of large actual area was deposited at a current density of 20.0 mA cm⁻². Amalgamated catalytic coatings were produced by immersing the cathode into 0.1 mol dm⁻³ HgCl₂ solution for 10-240 s.

The 1.0 mol dm⁻³ solution of Na₂SO₄ served as a basic electrolyte. Xylose concentration ranged from 0.2 to 1.6 mol dm⁻³. The experiments were performed at pH 7.0 and at temperatures of 20 to 80°C. The solutions were prepared with triple-distilled water and p.a. chemicals.

The cathodic current efficiency was determined by measuring the rate of hydrogen evolution. A graduated burette was placed over the cathode. The time required for the burette to fill up with the cathodically evolved hydrogen was measured.

Results and Discussion

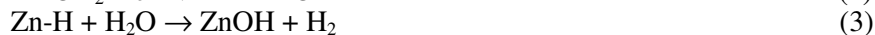
During the electrolysis of the xylose solution on the cathode, apart from the desired reduction of D-xylose to xylitol, several other reactions occur, including reduction of D-xylose to 1-deoxypentite, reduction of D-xylose to 2-deoxypentite and hydrogen evolution. D-lyxose is formed by isomerization of D-xylose. Isomerization and D-lyxose and D-xylose to deoxypentite reduction reactions practically do not

take place within the solution pH range of 6.0 to 9.0. Within this pH range, cathodic current losses are attributed only to hydrogen evolution (Jokić *et al.* 1991, Cvijović *et al.* 1998).

The cathode used was amalgamated zinc, due to a high overpotential for the hydrogen evolution reaction. The amalgam composition was selected in such a way as to maximally suppress hydrogen evolution and favour the reaction between the adsorbed hydrogen atoms and the adsorbed molecules of the oxycarbonyl form of D-xylose. The mercury content of the amalgam was dependent on the time of immersion of the zinc-coated electrode in the HgCl₂ solution. The experiment showed that current efficiencies were highest when the electrodes obtained by 60 s cementation were used.

Figure 1 shows polarization curves for the reaction of H₂ evolution from the 1.0 mol dm⁻³ solution of Na₂SO₄ at pH=7 and at temperatures of 20 and 80°C, respectively. The curves are S-shaped. A Tafel dependence with the slope of 120 mV is observed at low overpotentials. A limiting current is reached at higher overpotentials. The Tafel dependence with the slope of 120 mV again appears at potentials more negative than -1.8 V.

An analysis of the polarization characteristics of H₂ evolution and the evaluation of the Faraday impedance measurement results suggest that Zn-atoms covered with oxy-species and pure metallic Zn-atoms exist on the Zn(Hg) cathode within the potential range of -0.6 to -2.4 V (Trišović *et al.* 2001). At lower overpotentials, hydrogen is evolved on the surface Zn-atoms covered with oxy-species. The proposed H₂ evolution mechanism is as follows:



The reaction mechanism includes three consecutive elementary steps, i.e. two electrochemical steps and one chemical step (Jokić *et al.* 1991, Cvijović *et al.* 1998, Trišović *et al.* 2001, 2004). The mechanism entails the formation of an intermediary species, Zn-H, which is unstable and which reacts with an H₂O molecule at the chemical step to evolve H₂ and form the metal hydroxide again. The limiting current is dependent on the heterogeneous chemical reaction (3).

Hydrogen evolution on the metallic Zn surface occurs at potentials more negative than -1.8 V following the Volmer-Heyrovsky mechanism:



The limiting current for the heterogeneous chemical reaction (3) increases with increasing solution temperature (Figure 1). Up to -0.9 V (the potential of the onset of the limiting current region), the degree of the electrode coverage by the adsorbed hydrogen Zn-H is extremely low. Within the potential range of -0.9 to -2.1 V (the potential range of the limiting current), the coverage of the electrode by the adsorbed hydrogen increases as the potential becomes more

negative, reaching its maximum value at -2.1 V. The reaction of H_2 evolution on the metal surface occurs at extremely low degrees of coverage by the adsorbed hydrogen.

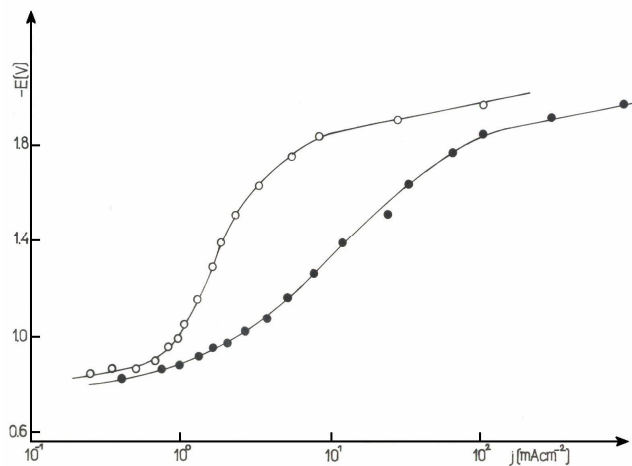


Fig. 1 Polarization curve for the hydrogen evolution reaction: ○-20°C; ●-80°C
(1.0 mol dm⁻³ Na₂SO₄; pH=7.0)

Figures 2 and 3 show polarization curves for the cathodic reactions of hydrogen evolution and xylose reduction from the 1.0 mol dm⁻³ solution of Na₂SO₄ in the absence (○) and presence of xylose in the solution (●) at t=20°C and t=80°C, respectively.

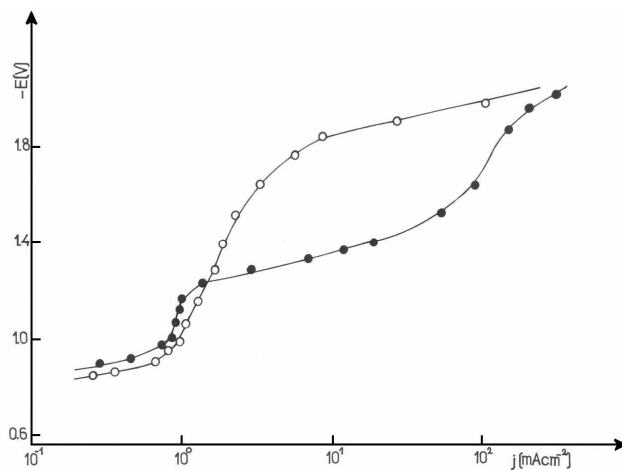


Fig. 2 Cathodic polarization curves: ○-1.0 mol dm⁻³ Na₂SO₄;
●-1.0 mol dm⁻³ Na₂SO₄ + 0.8 mol dm⁻³ C₅H₁₀O₅ (t=20°C; pH=7.0)

The above curves show that the cathodic reaction of hydrogen evolution is slightly inhibited by xylose within the potential range of up to -1.25 V. This indicates that xylose is most likely adsorbed only on the metallic surface and that it partially inhibits the H₂ evolution reaction by lateral interaction.

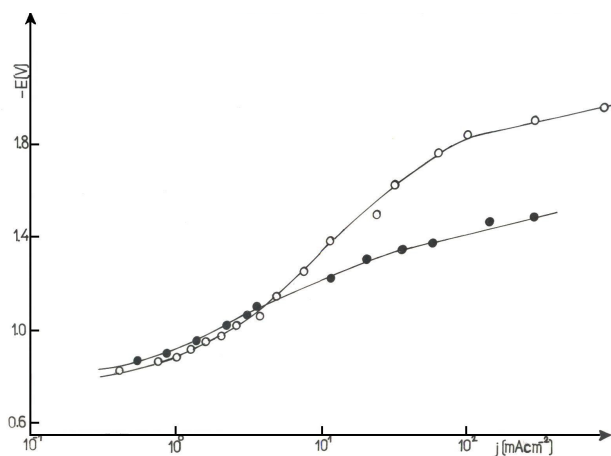
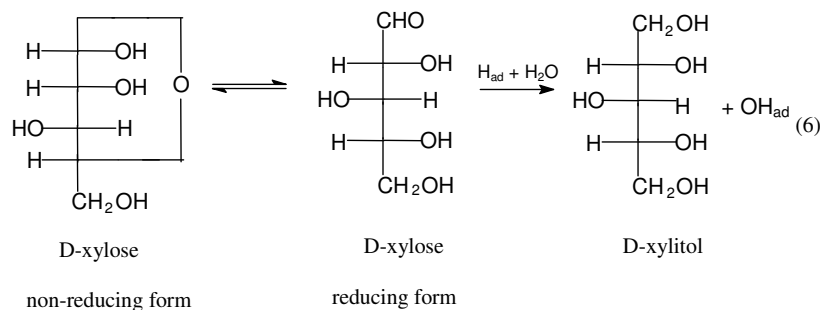


Fig. 3. Cathodic polarization curves: ○-1.0 mol dm⁻³ Na₂SO₄;
●-1.0 mol dm⁻³ Na₂SO₄ + 0.8 mol dm⁻³ C₅H₁₀O₅; (t=80°C; pH=7.0)

An equilibrium is established in the xylose solution between the cyclosemiacetal and oxycarbonyl forms. One form is converted into another by mutarotation. Only the aldehyde form of xylose is adsorbed and reacting on the cathode (Pork *et al.* 1985 Trišović *et al.* 2004).

Within the potential range of -1.25 to -1.8 V, the reduction currents in the presence of xylose in the solution are considerably higher than those in the absence of xylose. There is a Tafel dependence with the slope of 120 mV in the presence of xylose within the potential range of -1.25 V to -1.8 V. Within this potential range, xylose is reduced by the given reactions (1), (2) and (6), and the 120 mV slope suggests that the slow step is an electrochemical reaction. However, during the electrolysis of xylose at t=20°C within the potential range of -1.5 V to -2.0 V, cathodic limiting current is reached, suggesting that the slow step is, now, a heterogeneous chemical reaction between the adsorbed oxycarbonyl form of xylose and the adsorbed hydrogen and water molecule from the solution (reaction 6). Within the potential range of -1.5 to -2.0 V, the degree of coverage of the "oxy-zincate" electrode by the adsorbed hydrogen simultaneously increases (reaction 2). At potentials more negative than -2.0 V, hydrogen evolution on pure metallic zinc dominates (reactions 4 and 5).



An analysis of the above polarization curves (Figures 2 and 3) suggests that the current efficiency for xylitol production can be approximately calculated by the following equation:

$$\eta = \frac{I_k - I}{I_k} \quad (7)$$

where:

η – current efficiency for xylitol production,

I_k – cathodic current in the presence of xylose in the solution and

I – cathodic current in the absence of xylose.

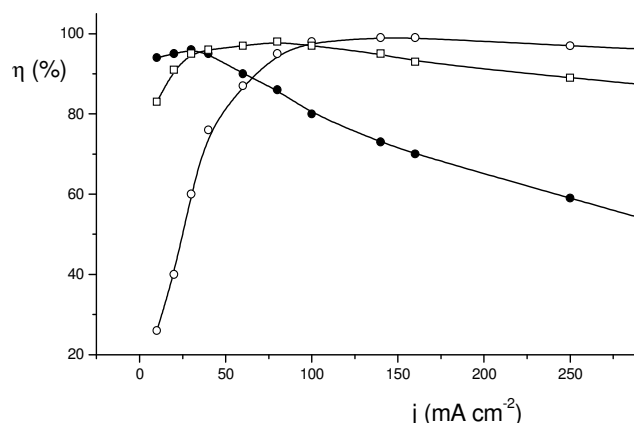


Fig. 4. Cathodic current efficiency for xylitol production plotted as a function of current densities and solution temperature: ●-20°C; □-40°C; ○-60°C (1.0 mol dm⁻³ C₅H₁₀O₅, 0.8 mol dm⁻³ KBr).

temperature (Figure 4). The experimentally obtained values given in Figure 4 are in good agreement with the values calculated by equation 7, confirming the adequacy of the

The equation (7) and the curves in Figures 2 and 3 indicate that the current efficiency for xylitol production increases with increasing current density, reaching its maximum and subsequently decreasing. The maximum shifts towards higher current densities as the solution temperature increases. This has been confirmed experimentally by measuring the dependence of the current efficiency for xylitol production on current density and solution temperature

proposed mechanisms of hydrogen evolution and xylose reduction on the amalgamated zinc used.

Conclusion

A procedure has been developed for the obtainment of an amalgamated zinc cathode to be used in electrochemical cells for the simultaneous production of xylitol and xylonic acid by electrolysis of xylose solution. The amalgamated zinc coating was formed by electrodeposition from sulfate solutions on a copper mesh. The amalgamated zinc of adequate concentration was prepared by immersing the coating in HgCl_2 solution for a specific period of time. The obtained cathode has good mechanical and electrochemical properties.

The study focused on examining the kinetics and proposing the mechanism of the parallel reactions of hydrogen evolution and xylose reduction on the amalgamated zinc in the Na_2SO_4 solution. At lower overpotentials, hydrogen is evolved on Zn atoms covered with oxy-species. The reaction mechanism involves three consecutive elementary steps, i.e. two electrochemical steps and one chemical step.

Xylose molecules are adsorbed only on metallic Zn. The adsorbed oxy-carbonyl form of xylose slightly inhibits the hydrogen evolution reaction by lateral interaction within the potential range of up to -1.25 V. At potentials more negative than -1.25 V, the adsorbed xylose molecules are reduced with Zn-H to xylitol. At potentials more negative than -2.0 V, H_2 evolution on the metallic Zn dominates. The cathodic polarization curves, in the presence or absence of xylose, are used to determine the cathodic current efficiency which is in good agreement with the values obtained by other methods.

The obtained experimental results have suggested that the developed amalgamated zinc cathode has good mechanical and electrochemical properties and that, as such, it can be used in industrial cells for xylitol production.

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KINETIKA ELEKTROHEMIJSKE REDUKCIJE KSILOZE NA AMALGAMU CINKA

- originalni naučni rad -

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Rezime

Tokom elektrolize vodenog rastvora ksiloze na katodi se paralelno odigravaju dve reakcije: redukcija ksiloze do ksilitola i reakcija izdvajanja vodonika.

Da bi se favorizovala željena reakcija redukcije ksiloze u ovom radu je redukcija izvođena na amalgamu cinka. Katalitička prevlaka amalgama formirana je na taj način što je izborom parametara elektrolize iz sulfatnog kupatila na baka-rnoj mreži najpre istaložena prevlaka cinka željenih karakteristika, a zatim zama-kanjem prevlake u rastvor HgCl_2 dobijen amalgam cinka odgovarajuće koncentracije.

Ispitivana je kinetika i mehanizam paralelnih reakcija izdvajanja vodonika i redukcije ksiloze na amalgamu cinka iz rastvora koji sadrži ksilozu i Na_2SO_4 kao osnovni elektrolit. Reakcija izdvajanja vodonika se odigrava preko dva paralelna mehanizma, i u prisustvu i u odsustvu ksiloze u rastvoru. Na nižim prenapetostima reakcija izdvajanja vodonika se odvija na oksidu cinka sa tri konsektivna elementarna stupnja. Heterogeni hemijski stupanj u kome učestvuje čestica Zn-H kontroliše ukupnu brzinu reakcije u oblasti granične struje. Na potencijalima negativnijim od $-2,0$ V reakcija izdvajanja vodonika se dominantno odigrava na metalnoj površini Folmer-Heirovskim reakcionim mehanizmom.

Ksiloza se adsorbuje na metalnom cinku. Na potencijalima negativnijim od $-1,25$ V adsorbovani molekuli ksiloze se reduju sa Zn-H do ksilitola. Na osnovu katodnih polarizacionih krivih u odsustvu i u prisustvu ksiloze određeno je katodno iskorišćenje struje po ksilitolu.