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Simultaneous electrolytic production of xylitol and xylonic acid from xylose*

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A new electrocatalytic process for simultaneous electrolytic production of xylitol and xylonic acid or the corresponding xylonate salts directly from α-d-xylose in alkaline solutions of neutral salt as supporting electrolyte has been developed and presented. An electrocatalytically active cathode coating with essentially hydridic features has been employed to enhance Faradaic yields in xylitol production at low current densities by heterogeneous reaction of hydrogenation with H-adatoms, and the entire mechanism has been proved by experimental evidence. An anionic selective anodic coating for titanium substrate was also used to suppress oxygen evolution and optimize the xylonic acid production by direct oxidation with anodically generated bromine, and to carry out the electrode process at almost equilibrium potential. The kinetic effect of specifically adsorbable anions for decreasing cathodic current yields in xylitol production and the resulting necessity for membrane separation of catholyte from anolyte, with proper optimization of the supporting neutral salt composition, has also been emphasized.

1. Introduction

Xylitol is a sweetener accepted by medical science and recommended for people suffering from diabetes. The classical chemical production route requires an energetically unsuitable industrial process proceeding catalytically (Raney–Ni doped with Mo) both at high pressure (above 80 bar) and temperature (353 K). Xylose originates from hydrolysis of various types of woods and other biomass derived raw materials.

A new electrochemical process has been developed for simultaneous production of xylitol and xylonic acid, or the corresponding xylonate salts directly from α-d-xylose in an undivided cell and preferably in an electrolyzer with cationic selective membrane [1, 2].

2. Experimental

Experiments have been carried out either in an undivided or membrane separated electrolytic cell made in lucite, both 1 dm^3 in volume and acting as back-mix flow reactors by the effect of a magnetic stirrer. Electrolyte was circulated and both thermostatted at 292 ± 0.5 K and pH-statted at pH 8.0 to 8.5. The electrolyte was basically 0.8 M KBr, 0.8 M α-d-xylose in twice distilled water and at pH between 7.5 and 8.0. In some experiments with the membrane divided cell, instead of bromide, the catholyte employed 0.8 M Na_2SO_4 as a neutral salt supporting electrolyte.

Two types of cathode were employed: amalgamated zinc and a catalytically active nickel or titanium coated electrode [3–5]. While amalgamated electrode was obtained by simple dipping of high purity zinc plate into 0.1 M $Hg(NO_3)_2$ for a short time (about 60 s), typical catalytic coating compositions were $MoFe_{3-x}Pt_x$ and $WFe_{3-x}Pt_x$, where x is between 0 and 3 (*cf.* [3–5]) and were produced by a combined electroless and electrodeposition method. An anionic selective anodic electrocatalytic coating of mixed oxide RuO_2/TiO_2 of rutile structure with a Pd/Sn intermetallic phase upon a titanium base substrate [6, 7] was used for the anode.

Two types of membranes were employed, DuPont "Nafion-400" and Asahi Glass "Flemion" membrane.

Experiments were carried out galvanostatically at constant current density and both cathodic and anodic current efficiencies were investigated as a function of xylose concentration (0.4 to 1.2 M α-d-xylose), current density (1.0 to 50 mA cm^{-2}), the anionic adsorption effect of catholyte, the effect of solution pH, and duration of electrolytic process. Cathodic and anodic current yields were controlled by both continuous gas

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rate recording and analysis of gaseous electrode products, and in parallel, by Waters 600E type HPLC (high performance liquid chromatography) monitoring of the conversion of xylose into xylitol. For α-d-xylose and its reduction products a column with cationic exchange resin was used, the latter being in calcium ionic form (Bio-Rad Laboratories HPX-87C). The column was thermostatted at 353 K with water as the solvent. On the other hand, a cationic exchange column with resin in the hydrogen form (Bio-Rad Laboratories HPX-89H) with an UV-detector (216 nm wavelength) was used for the analysis of the oxidation products within the anolyte. All products were identified by comparison of their retention times with standard commercial samples of known composition.

3. Results and discussion

3.1. *Features of the cathodic process*

Faradaic yields with amalgamated zinc depend both on the current density and xylose concentration (Fig. 1) and at low reaction rate the current efficiency approaches very high values, above 80 per cent in sulphate solution as used for the catholyte of the membrane separated cell, and up to 60 per cent in KBr electrolyte. The cathodic current efficiency in xylitol production decreases linearly with a low slope at low current density values and at a critical reaction rate, decreases sharply [8]. The Faradaic yield follows a similar dependence on concentration: over a low range of increasing xylose content the current efficiency increases and then levels off, while at higher current densities (above 20 and particularly at higher than 50 mA cm^{-2}), especially for low concentrations, it decreases abruptly [8]. These results imply that the reaction is mass-transport limited, but, there appears to be another limitation and a specific rate determining step of the overall cathodic process in xylitol production.

Cyclic voltammograms scanned with various concentrations of xylose exhibit mixed reduction of the latter into xylitol and simultaneous hydrogen evolution (Fig. 2). In other words, there are no peaks of xylose reduction to xylitol preceding hydrogen evolution, while the Faradaic yields approach the limiting value. Actually, the higher the current density, the lower the partial fraction of cathodic xylitol production. Thus, apparently the entire cathodic process is limited by the heterogeneous chemical reaction of xylose reduction by adsorbed H-adatoms (Scheme I), which depends on the rate constant and the coverage of the electrode surface, but does not appear primarily dependent on the electrode potential [8]. In fact, increasing of the cathode potential in the negative direction correspondingly increases the partial current of hydrogen evolution at higher current densities, when the rate of recombination of H-adatoms exceeds the hydrogenation rate of xylose to xylitol. Thus for xylitol production, there exists a certain limiting current detectable by measurements of xylitol yields, beyond which hydrogen evolution prevails.

Enyo [9] recently pointed out that organic species, which involve ionized forms of electroactive functional groups, before or after the reduction reaction, appear to undergo direct electrochemical reduction, while nonionized functional groups undergoing the reduction process, appear to be chemically hydrogenated by H-adatoms and obey typical heterogeneous electrocatalytic pathways. Such experimental evidence suggested the employment of a thin palladium foil tightly embedded in the cell wall instead of a membrane to act as the cathode at its surface facing the anode, while the opposite side, because of hydrogen intermetallic diffusion, acted as a source of adsorbed H-adatoms, ready for heterogeneous electroless catalytic reaction with dissolved xylose. Although the diffusion rate of hydrogen through palladium foil is slow and thus the rate determining step for such an electroless hydrogenation process, the production of xylitol from xylose is the best confirmation of the mechanism for the electroreduction processes already pointed out by Enyo [9]. Actually, organic synthesis has employed, for more than a century, hydrogen diffusion

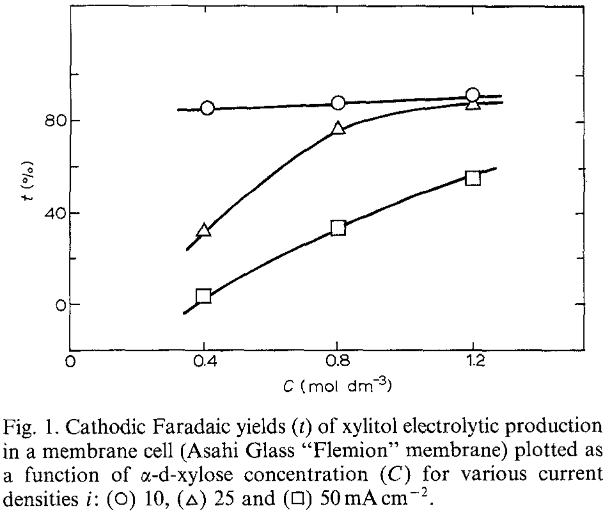


Fig. 1. Cathodic Faradaic yields (t) of xylitol electrolytic production in a membrane cell (Asahi Glass "Flemion" membrane) plotted as a function of α-d-xylose concentration (C) for various current densities i: (○) 10, (△) 25 and (□) 50 mA cm^{-2}.

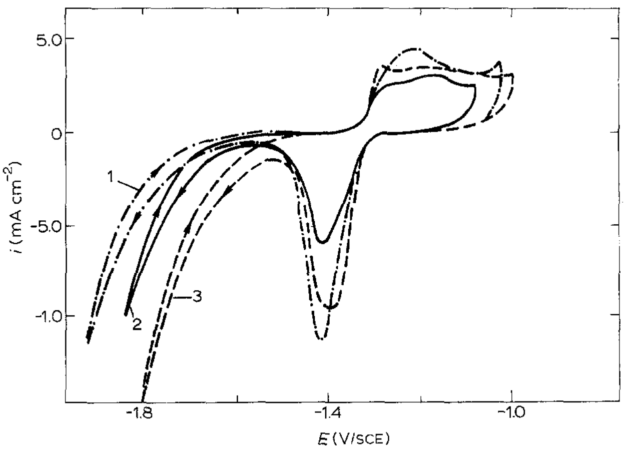
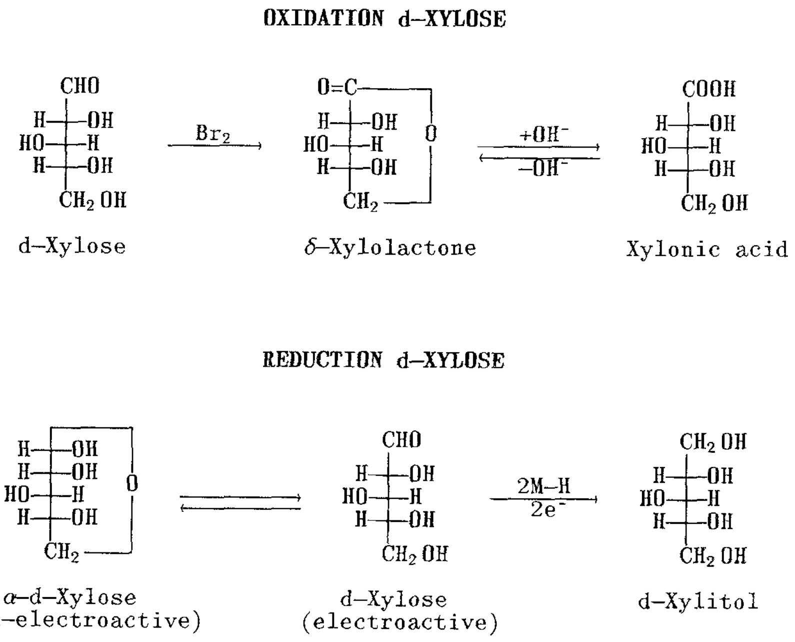


Fig. 2. Cyclic voltammograms of parallel behaviour of α-d-xylose and α-d-glucose upon Zn(Hg) electrode in alkaline (pH 8.5) 0.4 M KBr solution. Irreversible anodic and cathodic peaks at more positive potentials correspond to the oxidation of bromide ions into elemental bromine and to the reduction of hypobromite ions, respectively. Labels: (1) basic solution (0.4 M KBr), (2) 0.4 M α-d-glucose, 0.4 M KBr, and (3) 0.4 M α-d-xylose, 0.4 M KBr. Sweep rate 200 mV s^{-1}.



Scheme I. Cathodic and anodic pathways of α-d-xylose oxidation and reduction, respectively.

through palladium foils with the subsequent step of heterogeneous catalytic reduction or hydrogenation processes with various organic species.

This experiment, therefore, explains why there are no peaks for xylose cathodic reduction and why the cathodic xylitol production is limited more by the electrode surface, than by the mass transport of reacting species. This explains why there is no limiting current for xylose reduction, although there does exist a limiting current efficiency for cathodic xylitol generation. In fact, there is a limiting rate of xylitol production and since the current density increases further, its partial fraction apparently decreases.

Actually, there is a narrow range of mass transfer control when, at lower current densities, the concentration plays a definite role in enhancement of the Faradaic yields (Fig. 1). Thus engineering optimization primarily implies the extension of the cathode surface area, while the proper xylose content and an optimal flow rate represent contributions of secondary importance [8].

3.2. *Electrocatalytic effect of the cathodic coating*

Amalgamated zinc was previously employed in the similar cathodic process of sorbitol production from glucose [10], with the main aim of shifting hydrogen evolution to higher negative potentials and in such a manner as to provide higher current efficiency for the basic electroorganic reduction process regardless of the higher energy consumption. Actually, the electrolytic process as a whole was nevertheless performed at much lower overall energy consumption as compared with the classical industrial chemical process [10]. However, when it was realized now that the reduction of xylose occurs by heterogeneous catalytic reaction with adsorbed H-adatoms, any further application of amalgamated zinc was discontinued. Such experimental evidence suggested the application of highly active electrocatalysts for hydrogen evolution, which are otherwise characterized by both hydridic features [11, 12] and high coverage by H-adatoms [3–5]. It may appear controversial to apply an extremely highly active hydrogen electrode for cathodic hydrogenation of organic species, but a faster heterogeneous catalytic reaction is achieved with the latter, at least at lower electrode reaction rates, than the recombination of H-adatoms in hydrogen evolution. Finally, the experience with palladium electrode and palladium electroless hydrogenation directly suggest such possibilities, since it is also an extremely active electrode for hydrogen evolution.

It has been shown with both electrocatalytic coatings employed ($WFe_{3-x}Pt_x$ and $MoFe_{3-x}Pt_x$, as well as with the others where Co or Ni replace Fe, or Ru partially replaces Pt, *cf.* [3–5]), that there exists a current density range between 1 and 10 mA cm^{-2}, and even above the latter value, within which the heterogeneous reaction of xylose with adsorbed H-adatoms is distinctly faster and the predominating process as compared with the hydrogen evolution, which prevails at higher cathodic reaction rates [8]. Within such an optimal current density range, Faradaic yields for xylitol production were substantially higher, exceeding 90 per cent (Fig. 3). However, the main benefit comes from the electrocatalytic activity of the coating, which reduces the cathode potential considerably: at 10 mA cm^{-2} it was 1.1 V with reference to SCE as compared with 2.1 V for a Zn(Hg) electrode. This implies more than 25 per cent lower energy consumption as compared with typical electrochemical production (*cf.* [10]), besides the higher selectivity, which reflects in the higher current efficiency. However, as compared with the existing industrial process, which includes, the electrolysis of water for hydrogen supply for the hydrogenation reaction with xylose, the present

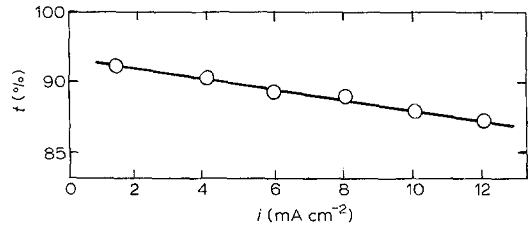


Fig. 3. The cathodic current efficiency (t) for xylitol production from alkaline (pH 8.5) 0.8 M α-d-xylose solution in 0.8 M Na_2SO_4 as the supporting electrolyte on electrocatalytically active (MoFe$_{3-x}$Pt$_x$) coating, deposited upon the titanium substrate by a combined electrolytic and electroless method (*cf.* [3–5]).

electrolytic process provides overall energy savings of more than 70 per cent (including contribution of the catalytically active anode, see below). There is also the simultaneous parallel anodic production of xylonic acid or xylonates with extremely high current yields, which shares the energy input with xylitol and makes the overall electrolytic process even more energetically favourable.

Synergetic electrocatalytic cathodic coatings [3–5] show high activity and pronounced hydridic features: note the reversible peak for hydrogen oxidation after its evolution and another peak for further oxidation of the catalyst surface in Fig. 4. These coatings have both high electrocatalytic activity for hydrogen electrodeposition as H-adatoms and also for the subsequent step of heterogeneous catalytic hydrogenation of xylose molecules by the latter. This is pronounced because of hydride formation and since the electrocatalysts behave with three-dimensional hydridic features [3–5, 11, 12].

3.3. *The anodic coating and the anodic process*

A titanium anode with RuO_2/TiO_2 and Pd/Sn intermetallic phase as the electrocatalytic coating [6, 7] has been employed for bromine evolution in an organic electrooxidation process, and has provided two achievements of substantial importance: (i) high anodic current efficiency (above 97 per cent) in xylonic acid production at almost equilibrium electrode potential, which implies nearly theoretical (thermodynamic) energy consumption and correspondingly reduced total energy losses, and (ii) a compact cell design as compared with the graphite anode, which also implies a dimensionally stable cell, unaltered hydrodynamic flow conditions, and constant cell voltage and overall energy consumption. The Pd/Sn intermetallic phase polarizes oxygen evolution and shifts its potential to much more positive values and hence behaves as the anionic selective electrocatalytic coating for bromine evolution (*cf.* [6, 7]). The anodic coating, originally developed for electrolytic chlorate and other halogenate production provides for suppression of the parallel reaction of the anodic hypobromite oxidation to bromate (the so called Foerster reaction of electrochemical bromate production [6, 7]), which otherwise proceeds accompanied with oxygen evolution. On the other hand, the high electrolyte pH (optimally between pH 8.0 and 8.5), and low temperature (293 K) effectively suppress the chemical conversion of hypobromite (or available bromine) into bromate (Foerster reaction of chemical bromate formation [6, 7]). Such electrode features contribute to higher Faradaic yields in the anodic oxidation of xylose to xylonic acid and, together with a highly reduced anodic overpotential, reduce the energy balance to more optimal level.

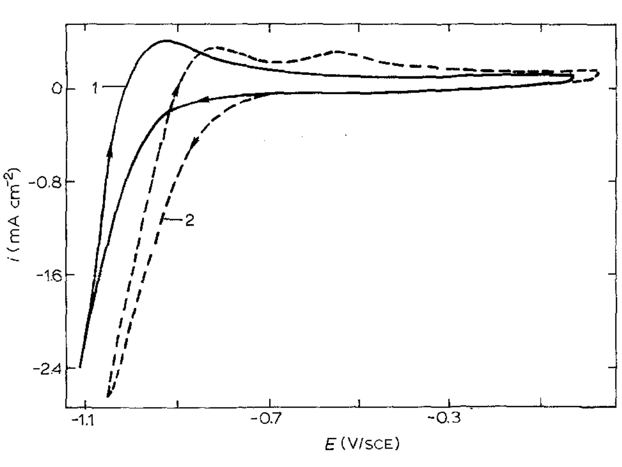


Fig. 4. Cyclic voltammograms of cathodic α-d-xylose behaviour scanned in alkaline (pH 8.0) sulphate solution on the electrocatalytically active (MoFe$_{3-x}$Pt$_x$) coating upon titanium substrate (*cf.* [3–5]). Labels: (1) plain 0.8 M Na_2SO_4 solution, (2) 0.8 M α-d-xylose, 0.8 M Na_2SO_4. Sweep rate 100 mV s^{-1}.

α-d-xylose undergoes oxidation with available bromine primarily in the vicinity of the anode surface and successively further in the bulk of solution (retention volume) first yielding an intermediate product, δ-xylolactone (Scheme I), which spontaneously undergoes further chemical conversion to xylonic acid. Such a typical homogeneous reaction predominantly occurs within the anodic diffusion layer, but also proceeds in the bulk of solution. It is visible by the intense colour of bromine in the electrolyte.

3.4. *Anionic effect on the cathodic current efficiency*

One of the far-reaching contributions and conclusions of the present work is that the specifically adsorbed anions (Br^-, I^-, and less so Cl^-) enhance the hydrogen evolution reaction, while the others, such as sulphate and perchlorate, increase the efficiency of xylitol production. Whereas in the presence of bromide the current yields never exceed 60 per cent, the sulphate supporting electrolyte enables Faradaic yields of xylitol above 90 per cent. This represents a highly practical result and, at the same time a theoretically important kinetic effect and contribution to the understanding of the relation between the electrode double layer structure and the resulting reaction kinetics and mechanism. Frumkin [13] has shown earlier that halide ions by virtue of their specific adsorption abilities increase the hydrogen evolution rate on a mercury cathode at lower current densities and explained the adsorption effect on the basis of changes in the double layer structure, and thereby

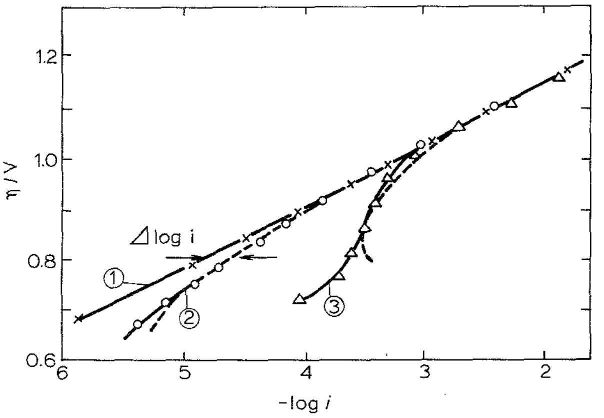


Fig. 5. Polarization characteristics (η against log i curves) for hydrogen evolution upon Hg electrode in 1 M HCl as the effect of various anionic species (1) chloride (2 M KCl), (2) bromide (2 M KBr), and (3) iodide (2 M KI)), on hydrogen overpotential (after Frumkin [13]). The dotted curves are calculated from curve 1 by means of the equation $(\Delta \log i/\Delta\varepsilon)_\eta \approx 0.5$, where ε is the charge density at the electrode surface [13].

reduced overvoltage. At higher cathodic reaction rates, and thence at more negative electrode potential values, when specific adsorption of anions ceases and repulsion of anions takes place, Tafel lines converge regardless of the type of anionic species (Fig. 5) and coincide with that for other nonadsorbing anions employed as supporting electrolytes.

Since electrocatalytically active hydridic coatings provide relatively high Faradaic yields only at lower current densities, the specifically adsorbable anions play a distinct role in the choice of electrolyte composition that enables high current efficiency. One has to avoid halogen and other specifically adsorbable anionic species and carry out the electrolytic process with sulphate or other supporting electrolytes, which essentially do not undergo any specific adsorption at moderate cathodic potentials.

Since bromide is substantially indispensable for anodic bromine generation and the subsequent step of α-d-xylose oxidation to xylonic acid, one can perform the entire electrolytic process in an undivided cell, but at lower cathodic current efficiency. Thus, for higher efficiency in the simultaneous production of both xylitol and xylonic acid it is of significance to separate catholyte from anolyte by a proper cationic selective membrane and to remove specifically adsorbable anions from the catholyte.

At relatively low temperature (293 K) and optimal pH range between 6.5 and 8.5, the interconversion reaction of xylose to lyxose is suppressed. Neither xylose reduction to 2-deoxyxylitol, nor to d-pentite can proceed. Lower temperature and optimal pH also suppress the chemical conversion of available bromine to bromate and actually shift the overall optimal pH range to between the pH values 7.5 and 8.5. The higher mutarotation rate of d-xylose relative to the same reaction of α-d-glucose provides the higher concentration of reducible aldehyde for further cathodic reduction (Scheme I) and favours the entire cathodic process of xylitol production as compared with the electrolytic process yielding sorbitol [8, 10].

The current losses in the cathodic process may originate from the reduction of α-d-xylose to 1-deoxypentite and, because of the isomerization of α-d-xylose to lyxose, as well as from further reduction of the latter to 2-deoxipentite; but, these reactions are practically negligible as compared with the parallel hydrogenation of α-d-xylose under the optimal process conditions.

Figure 2 shows that the cathodic reduction of α-d-xylose occurs at more positive potentials than α-d-glucose. The reduction of xylose is more pronounced because of the higher rate of mutarotation and thereby the higher resulting equilibrium concentration of the oxycarbonylic form of xylose than the corresponding concentration of the oxycarbonylic form of glucose for the same reaction. It is already well known that the amount of the reducible form for hexose sugars is usually much less than that for the corresponding configuration of pentose species, and the difference has been attributed to the stabilizing effect of the -CH_2OH group [8].

A steady-state production at optimal the current density, the reacting α-d-xylose contents and electrolyte composition, temperature and the pH value, provides essentially constant Faradaic yields independent of the duration of the electrolytic process. The separation of cathodic and anodic products from the catholyte and anolyte are the subject of engineering optimizations and will be presented elsewhere [8].

4. Conclusion

A new electrocatalytic process for simultaneous electrolytic production of xylitol and xylonic acid or the corresponding xylonate salts directly from α-d-xylose in alkaline solutions of neutral salt as supporting electrolyte has been developed and optimized. The process arises favourable in energy consumption and substantially exceeds the classical industrial production in that respect because of two parallel achievements: (i) Remarkably reduced cathodic overvoltage by extremely active cathodic electrocatalytic coating and (ii) Substantially increased Faradaic yields for xylitol production by the high selectivity hydrogenation process at the cathodic coating at low current densities. The high activity and selectivity of the anodic coating contributes in addition to the other part of energy saving, too. Thence, from the energy consumption point of view, the present process of simultaneous xylitol and xylonic acid production from xylose would contribute to remarkable advances in industrial production.

Acknowledgements

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