

Short communication

Application of hydrogen-storage alloy electrode in electrochemical reduction of glucose

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Abstract

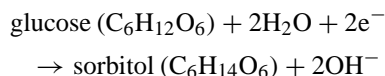
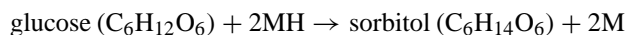
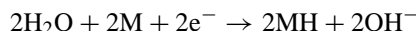
Electrolysis of glucose was performed at constant potential using hydrogen-storage alloy as catalytic reduction electrode. A superficial treatment and activation of the hydrogen-storage alloy powder had an obvious effect on improving the current efficiency for the generation of sorbitol. The most favorable results were obtained when a current density of 8 mA cm^{-2} , a voltage of 4.0–5.0 V and a pH of 8 at a temperature of 30°C are used. Prior to use the electrode was treated for 2 h at 80°C with a solution containing KBH_4 (0.5 mol/l), KF (0.5 mol/l) and KOH (6 mol/l). Under optimized conditions the current efficiency for sorbitol by electrolyzing glucose exceeded 90%. The yield of sorbitol was around 80%. The lifetime of the electrode was tested and analyzed, and methods of regeneration are discussed.
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Keywords: Hydrogen-storage alloy electrode; Sorbitol; Glucose; Catalytic reduction

1. Introduction

Sorbitol is an important industrial compound. It is used in synthetic fiber production, food additive, synthetic resin, leatherette and detonator. Moreover, it is widely applied in the field of medicine, and in the food and fine chemical industry. At present, the main route of sorbitol production is the catalytic hydrogenation of glucose. This process is operated at high temperature and high pressure, therefore appropriate equipments are necessary. Recently, attention has been paid to the synthesis of sorbitol by electrolyzing glucose, due to the increasing application of electrochemical syntheses [1–3]. There are a few references for the preparation of sorbitol by electrolytic reduction of glucose using Pb and Zn(Hg) cathodes [4,5]. However, the Pb and Zn(Hg) electrodes, due to the soft properties of the metals and their low mechanical resistance, show serious cathodic corrosion. Consequently, cathodic dregs are produced and it is difficult to separate the products. Moreover, both Pb and Zn(Hg) are poisonous. The resulting products cannot be applied in medicine and food production. Presently, hydrogen-storage alloy is rapidly developed and widely

applied, but there are no reports on preparation of sorbitol using a hydrogen-storage alloy reduction electrode [6,7]. There is catalytic as well as electrochemical hydrogenation within the electrolytic reduction of glucose [8]:



Herein we report on the preparation of sorbitol by electrolyzing glucose using a hydrogen-storage alloy electrode.

2. Experimental

2.1. Starting materials and devices

Glucose, Na_2SO_4 and KOH were used as commercially available reagents. $(\text{La}_{0.68}\text{Ce}_{0.17}\text{Pr}_{0.05}\text{Nd}_{0.10})\text{Ni}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.40}\text{Al}_{0.30}$ mixed rare earths hydrogen-storage alloy powder was prepared according to the method reported in the literature [9].

The plexiglass electro bath is equipped with F-101 cation exchange membrane. The hydrogen-storage alloy electrode

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is used as cathode with a stirrer in the cathodic chamber. The stirring rate is 200 r/min. The anode is made out of a plumbago block with a length of 5 cm, width of 5 cm and thickness of 1 cm.

2.2. Preparation of hydrogen-storage alloy electrode

2.2.1. The surface treatment of hydrogen-storage alloy powder

The hydrogen-storage alloy powder was treated according to the following three procedures and washed with distilled water. Finally, the three different hydrogen-storage alloy powders (I–III) were obtained after drying in vacuum: (I) stirring for 2 h at 80 °C in a solution containing KBH_4 (0.5 mol/l) and KOH (6 mol/l); (II) stirring for 2 h at 80 °C in a solution containing KBH_4 (0.5 mol/l), KF (0.5 mol/l) and KOH (6 mol/l); (III) no additional treatment.

2.2.2. Preparation and activation of the hydrogen-storage alloy electrode

The treated lanthanum rare earth hydrogen-storage alloy (2.0 g) was mixed with Ni (0.5 g) powder and added to 1 ml of a solution of 2% PVA (polyvinyl alcohol). The resulting alloy powder was equally daubed on the vesicant Ni after stirring for 0.5 h. Finally, the mixture of alloy powder was covered using a solution of 2.5% PTFE. After drying the resulting vesicant Ni was pressed to a module. The electrodes (I–III) were obtained along this method. In order to reach constant electrode conditions, the electrodes (I–III) are charged and discharged five times at 60 mA/g current. Each time the electrodes were charged for 6 h and discharged to 0.64 mV versus the Hg/HgO electrode. The electrodes were immersed in a solution of glucose (0.5 mol/l) for 24 h before use.

2.3. Electrolysis

Glucose of 200 ml (1.0 mol/l) and 200 ml Na_2SO_4 (0.5 mol/l) electrolyte were filled in the cathodic part of the electrolytic cell, whereas 200 ml of KOH (2.0 mol/l) were given in the anodic chamber. A F-101 cation exchange membrane was used between the cathodic and the anodic chamber. Finally, the electrolysis cell was kept at constant temperature using a water bath. The electrolyte in the anodic chamber was circulated using a LDB-H squirring pump. Voltage control was achieved by a HDV-7 transistor

equipped with constant potentiometer. The resulting product was analyzed by high performance liquid chromatography (HPLC).

The lifetime for the hydrogen-storage alloy electrode was determined when the electrolysis current efficiency of glucose was less than 30%. The reason for the decrease of efficiency of the electrode was investigated using DTA and SEM. The used electrodes were regenerated.

3. Experimental results and discussion

3.1. Optimization of electrolysis conditions

3.1.1. Effects of the surface treatment and the activation on the current efficiency

The effects of the surface treatment and the activation of the electrodes on the current efficiency are shown in Table 1. The electrolysis was conducted for 10 h under the following conditions: the current density was 4 mA cm^{-2} , the space between electrodes 3 cm, the applied voltage 4.5 V, the concentration of glucose 1.0 mol/l and that of Na_2SO_4 0.5 mol/l, at a temperature of 30 °C.

The experimental results indicate that the electrode II had the best performance in terms of catalyzing capacity and durability. This might be due to the fact that at high temperatures the oxides of Al, Mn, and La within the alloy are partly dissolved or reduced and Ni-enriched layers are preferentially formed after the alloy was treated with alkali and KBH_4 [10]. Hence the efficiency of the surface area increased. A layer of fluoride film is formed on the surface after adding KF. This layer prevents the oxidation of the alloy and improved the antioxidation ability [11]. Consequently, the changes of the alloy surface directly affected the electrode activation, the hydrogen adsorption and the catalysis. Moreover, the capabilities of activated hydrogen-storage alloy were better than those without activation. The reason that the capabilities of hydrogen absorption and storage of none activated alloy were poor is mostly due to the hydrogen atoms converted to hydrogen gas evolved at the surface. In contrast, the electrodes which were activated a few times could absorb hydrogen under swelling and increasing the efficiency through additional surface area. The catalyzing capability was improved, and hydrogen absorption enhanced [12,13]. Therefore, electrode II was used preferentially as a study electrode.

Table 1
The effect of superficial treatment and activation on the current efficiency

	Electrode I		Electrode II		Electrode III	
	Used 1st time	Used 10th time	Used 1st time	Used 10th time	Used 1st time	Used 10th time
The current efficiency of the activated electrode (%)	87	70	88	86	80	67
The current efficiency of the non-activated electrode (%)	50	56	52	60	30	57

Table 2
The effects of the current density on the current efficiency

Current density (mA cm ⁻²)	Bath voltage (V)	η (%)
4	4.0	82
8	4.8	92
16	5.6	81
20	7.2	62

η stands for current efficiency of sorbitol.

3.1.2. Effects of the current density on the current efficiency

The electrolysis conditions are the following: the study electrode was the hydrogen-storage alloy electrode II with an efficacious area of 5 cm × 5 cm, the current density was changed according to Table 2, and the other parameters were kept constant.

The current density of 8 mA cm⁻² was suitable, otherwise when it was increased, a large number of hydrogen atoms could not be absorbed in time and hydrogen gas was evolved. Consequently at the same time, the bath voltage rose and the consumption of energy increased. Apart from that when the current density was too low, the time of electrolysis was prolonged and it was not likely to reach the deoxidation voltage and the high current efficiency.

3.1.3. Effects of temperature on the current efficiency

A current density of 8 mA cm⁻² was maintained for 6 h at 20, 30, 40, and 50 °C, respectively. The other conditions are the same as those reported in Section 3.1.1. The results are listed in Table 3.

The data in Table 3 clearly show that the effect of temperature on the current efficiency is remarkable. The sorbitol current efficiency increased when the temperature was raised from 20 to 30 °C and decreased from 30 to 50 °C. To examine whether there are any impurities produced, the products of electrolysis were analyzed using high performance liquid chromatography at various temperatures. It was found that there was more mannitol formed at higher temperature. Therefore, the temperature should be maintained at 30 °C.

3.1.4. Effects of pH on the current efficiency

The effect of the pH on the current efficiency was studied at various pH values with the current density of 8 mA cm⁻² and the temperature of 30 °C. The other conditions are the same as those reported in Section 3.1.1. The results are listed in Table 4.

The current efficiency for sorbitol was quite high and steady when the pH was about 8. There was also a high

Table 3
The effect of temperature on the current efficiency

Temperature (°C)	Current density (mA cm ⁻²)	Bath voltage (V)	η (%)
20	8	5.6	67
30	8	4.8	92
40	8	4.2	90
50	8	3.6	82

Table 4
The effect of pH on the current efficiency

pH value	Bath voltage (V)	η (%)
4.7	4.4	86
7.0	5.0	72
8.4	4.8	92
9.8	4.2	94
11.2	3.6	95

current efficiency at pH 11, however, the glucose was easily converted to fructose under strong alkaline conditions and thus mannitol and deoxidized sorbitol impurities were formed [5]. Therefore, the pH should be kept at about 8.

3.2. The lifetime of hydrogen-storage alloy electrodes

The current efficiency of the primary electrode used after activation was compared with that of the electrode used after 20 turnovers. The results show that the current efficiency drops to 32% after the electrode was used 20 times. It is likely due to the poisoning of the catalyst. There are two main reasons that catalyst poisoning occurs, firstly the crystal phase of the alloy has changed, and secondly the surface of the catalyst has adsorbed some impurities [14,15]. Therefore, additional physical methods were used.

3.2.1. SEM analysis

Two kinds of electrode surfaces were investigated using SEM: firstly, the primary electrode after activation and secondly, the electrode after 20 runs. From Fig. 1 it is obvious that the alloy grains of the first electrode have a rough surface and are stacked tightly together. Therefore, the high active surface has the advantage of generation and absorption of hydrogen. Whereas from Fig. 2 it can be seen that the electrode surface becomes smoother and the grains are agglomerated, which resulted in the decrease of catalyst and reactants contact area. Finally, at the same time the area of the new highly activated electrode surface decreases due to the deposition of glucose residue on the alloy surface.

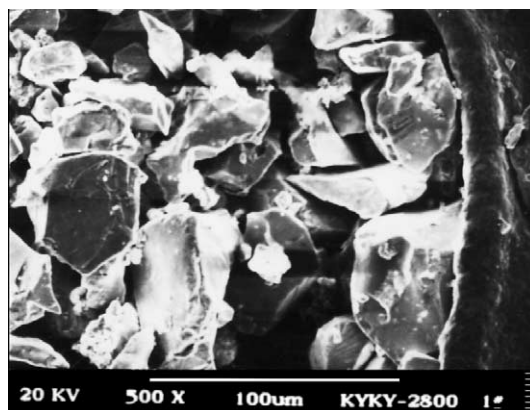


Fig. 1. Primary hydrogen-storage electrode used after activation.

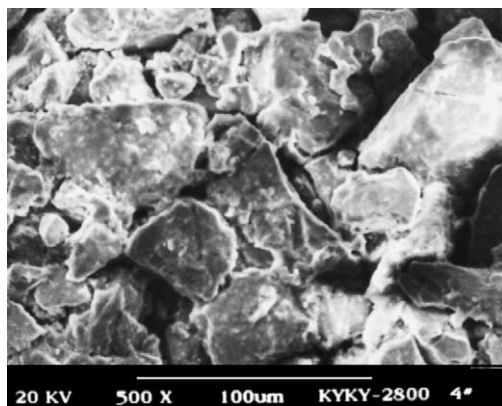


Fig. 2. Hydrogen-storage electrode used after 20 runs.

3.2.2. DTA analysis

In order to find out whether the decrease of electrode catalyzing activation resulted from a change of the crystal phase or is due to the absorption of polymeric impurities, the DTA analysis was used for both electrode alloys. A TAS100 DTA analysis instrument with samples under N_2 was used.

From Fig. 3, we learn that there is an endothermic peak in the DTA curve of the alloy. The endothermic temperature is about $220^\circ C$ and it does not change on the whole before and after using the alloy. This shows that the crystal phase did not change before and after the electrode is used under the experimental conditions. The decrease of electrode activation resulted from the absorption of impurities, which covered the active center of the electrode [5,15]. The activated capability recovers after removing the adsorbed impurities.

3.2.3. Regeneration of the hydrogen-storage alloy electrode

Three kinds of treatment were chosen for the regeneration of the hydrogen-storage alloy electrodes. Firstly, heating the electrode to $80^\circ C$ in a solution of 20% KOH and keeping the temperature over a period of 2 h, after cooling to room temperature the electrodes were treated with distilled water till the pH reached nearly 7. Secondly, the electrodes were

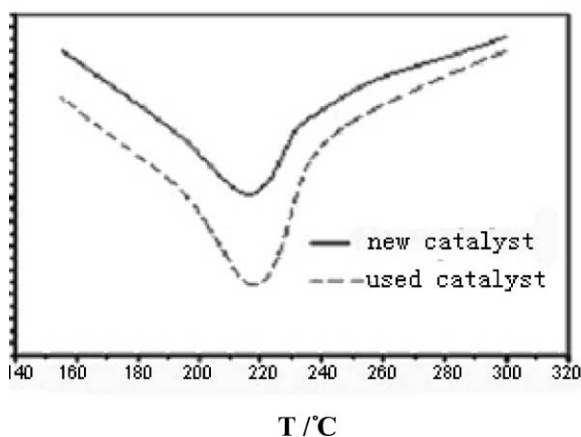


Fig. 3. DTA analysis.

Table 5
The experiment of the electrode regeneration

Condition	Temperature ($^\circ C$)	Time (min)	Current efficiency (%)
20 wt.% KOH	80	120	82
Distilled water	80	120	30
No treatment	–	–	32

treated with distilled water at $80^\circ C$ for 2 h. Thirdly, there was no additional treatment of the electrodes. The results are summarized in Table 5.

It was found that the treatment with hot KOH solution was by far the best. The current efficiency of sorbitol still reached over 80% after the regeneration of the electrode. The key for the catalytic behavior of the electrode is the enrichment of the surface with lanthanum and nickel. Obviously, those oxides prevent adsorption and formation of hydrogen. We assume that Al, Mn and other oxides at the electrode surface are dissolved after treatment with hot alkali that leads to a new enriched nickel surface layer with a high catalytic activity.

4. Conclusions

The hydrogen-storage alloy electrode is a highly active catalytic system. The surface treatment and the activation of the electrode greatly improved the catalytic activity and the number of cycles.

The optimal conditions for sorbitol preparation by electrolyzing glucose with the alloy electrode are reached, when a current density of 8 mA cm^{-2} , a voltage of 4.0–5.0 V at a temperature of $30^\circ C$ and a pH of 8 is used. Moreover, the electrode was treated for 2 h at $80^\circ C$ with a solution containing KBH_4 (0.5 mol/l), KF (0.5 mol/l) and KOH (6 mol/l). Under these conditions, the current efficiency of sorbitol was over 90% and the glucose invert rate of about 80%.

The adsorption of some impurities at the electrode surface leads to a decrease of the current efficiency and a shorter lifetime of the electrode. Nevertheless, the current efficiency of sorbitol still reached over 80% after reborn treatment of the electrode with hot KOH solution.

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