



Preliminary study on zinc–air battery using zinc regeneration electrolysis with propanol oxidation as a counter electrode reaction

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ABSTRACT

A zinc–air battery using zinc regeneration electrolysis with propanol oxidation as a counter electrode reaction is reported in this paper. It possesses functions of both zincate reduction and electrochemical preparation, showing the potential for increasing the electronic energy utilization. Charge/discharge tests and scanning electron microscopy (SEM) micrographs reveal that when a nickel sheet plated with the high-H₂-overpotential metal, cadmium, was used as the negative substrate electrode, the dendritic formation and hydrogen evolution are suppressed effectively, and granular zinc deposits become larger but relatively dense with the increase of charge time. The performance of batteries is favorable even if the charge time is as long as 5 h at the current density of 20 mA cm⁻². Better discharge performance is achieved using a ‘cavity-opening’ configuration for the discharge cell rather than a ‘gas-introducing’ configuration. The highest energy efficiency is up to 59.2%. That is, the energy consumed by organic electro-synthesis can be recovered by 59.2%. Cyclic voltammograms show that the sintered nickel electrode exhibits a good electro-catalysis activity for the propanol oxidation. The increase of propanol concentration conduces to an enhancement in the organic electro-synthesis efficiency. The organic electro-synthesis current efficiency of 82% can be obtained.

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1. Introduction

At present, energy sources tend to be increasingly short, particularly for electricity supply. This is primarily resulted from a rapid increase in those industries that consume electrical energy considerably such as aluminum electrolysis, chlorine alkali, organic electro-synthesis and so on [1]. Thus, energy and electricity conservation are of critical importance. In addition to energy-saving and energy-consumption-lowering, one key approach for solving this problem is the reinforcement in the development and utilization of renewable energy such as solar or wind [2]. To ensure the stable supply of renewable energy, it is necessary to develop an energy storage technology showing high energy efficiency, low cost, environmentally benign, as well as safety and reliability. In the case of load-leveling/peak-shaving, such energy storage technology is also needed [2]. Among all kinds of energy storage batteries, given their unique performance characteristics, redox flow batteries are regarded as the most efficient and reliable storage media suitable for large-scale energy storage applications [3].

Since the redox flow battery concept was first proposed by Thaller [4], a number of available redox flow battery systems have been fabricated and developed through changing two redox couples [5]. In general, redox flow battery systems can be divided into the liquid-phase and deposit-type energy storage systems according to the mechanism of energy storage. Comparatively, the liquid-phase energy storage systems have been studied more widely [3]. However, all of the above systems require the employment of cells with membranes. Such membranes are expensive, increase the complexity and cost of cells and give rise to the cross-contamination of positive and negative electrolytes. This has led researchers to investigate a deposit-type energy storage system, which is based on the deposition/dissolution of metal ions which are highly soluble, and in which there is no requirement for a membrane. Recently, it has attracted increasing attention. For example, a lead acid flow battery based on Pb²⁺/Pb and PbO₂/Pb²⁺ was reported by Pletcher and co-workers [6] in 2004. A novel redox flow battery, single flow zinc–nickel battery was proposed by us [7]. In this battery, the electrical energy storage is realized by deposition/dissolution of zinc in flowing electrolytes, utilizing the high stability of nickel oxides and the relatively high solubility of zinc oxides in an alkaline medium. In addition, the use of the deposit-type zinc electrode in flowing electrolytes provides an approach to reduce the tendency towards shape-change, dendrite growth, and passivation.

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High specific energy, low cost and environmental friendliness are some of the outstanding merits of a Zn/air energy system. In early days, Zn–air batteries had received widespread great attention [8,9]. Unlike other batteries, the zinc–air battery is anode–electrolyte limiting. That is, the active electrode material of the battery, oxygen, is taken from the surrounding air and reduced electrocatalytically at a non-consumable electrode. And so, the air cathode possesses long life in terms of ampere hours. Theoretically, it can be used again and again with fresh zinc and alkali each time. Most of commercialized zinc–air batteries are currently small coin-type or large square-type zinc–air primary cells, which are discarded after used one time [10]. Since the 1960s–1970s, considerable work and great efforts have been carried out extensively to develop rechargeable zinc–air batteries for possible application in electric vehicles [11]. However, as a secondary system, although it is more convenient, the zinc–air battery is still seriously limited.

In organic electrochemical industry, organic compounds are reduced or oxidized through the transfer of electrons on electrodes to obtain aimed products. Hence, the electro-organic synthesis is one kind of green synthetical technology with high added value. In recent years, the organic electro-synthesis industry has grown rapidly [12,13]. However, for organic electro-synthesis, in general, products can only be obtained on one electrode, and electricity is synchronously wasted in the form of side reactions on the other electrode. Although there is a paired electro-synthesis technology emerging in which the anodic and cathodic reactions are utilized simultaneously, it is only applied for some special organic reactions. It is indicated by literatures [14,15] that the electrical energy consumed by organic electro-synthetical industry accounts for almost 50–70% of cost, which has become a considerable obstacle for further development of the organic electrochemical industry. In essence, the organic electro-synthesis is similar to the charge process of redox flow batteries, in which cathodic products with low valence and anodic products with high valence are electro-synthesized. The storage of the electrical energy passed through a counter electrode in the process of electro-organic synthesis is of important significance.

Based on comprehensive consideration of above three electrochemical systems, we propose a novel system, zinc–air battery using zinc regeneration electrolysis with propanol oxidation as a counter electrode reaction, in which ‘zincate reduction’ and ‘propanol oxidation’ are combined. During charge, one target organic product, propanoic acid, is obtained on the positive electrode, and meanwhile, the quantity of electricity passing through the negative electrode is stored by deposited zinc. During discharge, an air electrode where oxygen is fed from the air is employed on the positive electrode to combine with the zinc electrode, forming another cell to deliver energy. As a result, dual roles of electro-synthesis and energy storage can be achieved as a battery is charged

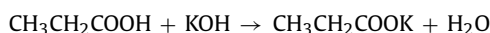
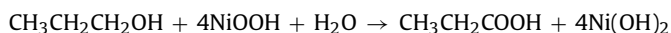
one time. So, the electrical energy utilization can be enhanced effectively.

In this paper, we shall describe the chemistry, electrochemistry and performance of this novel system based on the electrode reactions of Zn(II) in concentrated alkaline solution, in which the propanol is employed as an organic raw material. The propanol oxidation is an example of electrochemical oxidation reaction in the zinc regeneration process and industrially more important reactions will replace it in the practical electrolysis process. During electrolysis, the electrode reactions are

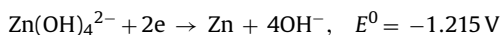
anode [16]:



chemical reactions:

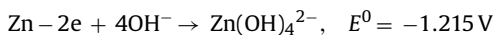


cathode [16]:



Then, the electricity passed through the cathode is stored in the reduced species of Zn. At the same time, the organic product, propanoic acid, is obtained on the anode.

During discharge, the anodic reaction is as follows [16]:



Oxygen from the air reacts with the alkaline aqueous solution is as follows [16]:

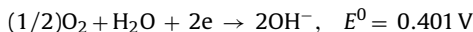


Fig. 1 shows the configuration of this zinc–air battery using zinc regeneration electrolysis with propanol oxidation as a counter electrode reaction. This system consists of two cells connected with a zinc electrode in flowing electrolytes and used for electrolysis and discharge, respectively. The cell for electrolysis processes is sealed. It is comprised of two compartments separated by an ion-exchange membrane. Each compartment is connected to a reservoir tank and a pump through an electrolyte circuit loop. Sintered nickel electrodes are employed as positive electrodes, and inert metal current collectors are employed as negative substrate electrodes. The alkaline aqueous solution of propanol and concentrated KOH solution of ZnO contained in separate storage tanks are circulated through the electrolysis cell where the reactions (oxidation and reduction)

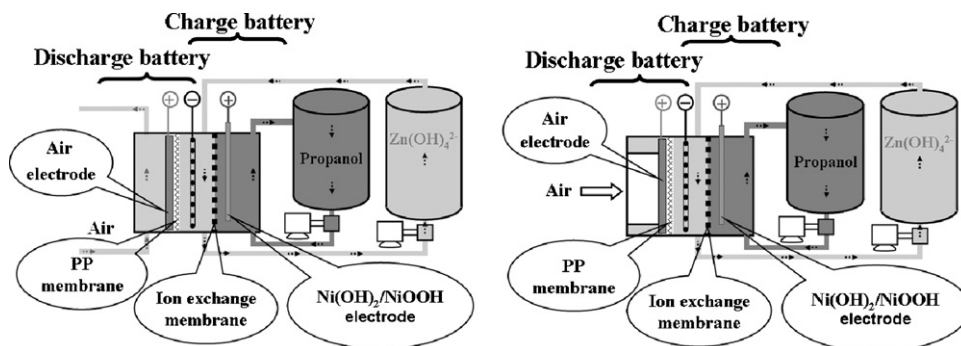


Fig. 1. The configuration of a zinc–air battery using zinc regeneration electrolysis including a gas-introducing (A) and a cavity-opening (B).

take place. On the positive electrode, Ni(OH)₂ is oxidized to NiOOH which chemically oxidizes propanol into propanoic acid [17,18]. On the negative electrode, zincate ions are reduced to zinc, continuously being electroplated onto the inert metal substrate. Hence, the cross-contamination between anodic and cathodic electrolytes is expected to be lowered significantly. Specially, the dendrite growth and shape-change associated with the zinc electrode might be inhibited effectively due to the flowing electrolytes, and no stratification occurs in the electrolytes. Then, the organic product, propanoic acid, is obtained on the positive electrode. And, energy on the negative electrode is conserved. The cell for discharge processes is comprised of one liquid and one gas compartment. They are separated by a porous poly-propylene membrane. On the positive electrode, an air electrode is employed instead of a sintered nickel electrode. A 'gas-introducing' configuration (see Fig. 1(A)) and a 'cavity-opening' configuration (see Fig. 1(B)) are used to introduce the air. In the case of the 'gas-introducing' configuration, air is fed at a pressure slightly higher than the atmosphere pressure by a tiny air compressor. This cell configuration is a sealed one. In the case of the 'cavity-opening' configuration, a square cavity with an area of 5.5 cm² is placed on the positive stainless steel end plate, making the air electrode to contact directly with the air. Thus, this cell configuration is an open one. The concentrated KOH solution of ZnO is withdrawn from the separate storage tank and fed into the liquid compartment. Air enters the gas compartment. The deposited zinc reacts with oxygen in such a way that voltage is generated between two electrodes. The dissolution reaction of zinc occurs in a circulating solution and the cathodic reaction occurs in a chemical mediator known as an air electrode. The end of the discharge occurs when all the deposited zinc is consumed. Regeneration of the zinc is performed in the electrolysis cell which is shown as a separate entity.

In this system, the battery performance is influenced greatly by the zinc deposition behavior. The zinc deposition in alkaline zincate solutions has been previously reported. Popov and Keca [19] discussed the electrodeposition of zinc from alkaline zincate solutions on copper. It was also reported that copper current collectors were coated with a high-H₂-overpotential metal, such as Pb, Cd, In, Sn, or Bi to prevent Cu dissolution during overdischarge [20].

In the present work, a nickel sheet coated with Cd was selected as the substrate electrode to explore the effects of the zinc deposition behavior on the charge/discharge performance of the battery. On top of it, the anodic reactions during electrolysis are investigated systemically mainly in terms of organic electro-synthesis efficiencies. At the same time, a small test device is fabricated to demonstrate the principle of the zinc-air battery using zinc regeneration electrolysis with propanol oxidation as a counter electrode reaction.

2. Experimental

2.1. Preparation of cadmium-plated nickel substrate electrodes

After grinding with 800[#] sand papers, a nickel sheet (dimension: 2.5 cm × 2.2 cm) was cleaned with acetone and then washed by ultrasonic cleaning in deionized water for 15 min prior to electroplating. And then, cadmium was electroplated on the newly treated nickel sheet (Shanghai Metallic Strip and Foil Corp., China) by constant and square-wave pulsating overpotential at the current density of 20 mA cm⁻² for 15 min [21] at room temperature in a two-electrode open cell. The counter electrode was a large flexible graphite plate. The electrolyte used was an aqueous solution containing 32 g L⁻¹ CdCl₂·5/2H₂O, 110 g L⁻¹ NH₄Cl, 120 g L⁻¹ N(CH₂COOH)₃, 37 g L⁻¹ (NCH₂)₂(CH₂COOH)₄ and 20 g L⁻¹ CH₃COONH₄. During electrolysis, the cell voltage was kept at

around 3.0 V. Consequently, the cadmium-plated nickel substrate electrode was obtained.

2.2. Electrochemical analysis and physical-chemical characterization

The electrochemical experiments about the propanol oxidation at a nickel electrode were performed by cyclic voltammetries (CV) in a three-electrode cell. The working electrode (area: 0.196 cm²) was constructed from a nickel rod (purity >99.9%) and was in the form of a disk electrode with a PTFE sheath. A sintered nickel sheet and Hg/HgO were employed as counter and reference electrodes, respectively. The sweep range was from 0.1 V to 0.65 V vs. Hg/HgO electrode at 10 mV s⁻¹.

Tests on the electro-catalysis characteristic of a sintered nickel electrode (Jiangsu Highstar Group Co. Ltd., China) were carried out by cyclic voltammetry (CV) between 0.1 V and 0.7 V vs. Hg/HgO electrode at 1 mV s⁻¹ and 5 mV s⁻¹. The CV experiments were conducted using a three-electrode cell which comprised a sintered nickel electrode as the working electrode (area: 0.12 cm²), with a nickel sheet and Hg/HgO as counter and reference electrodes, respectively.

All of the cyclic voltammograms were measured by the CHI1100A electrochemical station (CH Corporation, USA).

The surface characterization of zinc deposits was investigated by a scanning electron microscope (SEM, Cambridge S-360). The treatment of deposited zinc electrodes was described in the literature [22].

2.3. Fabrication of charge/discharge separated batteries and performance measurements

A cadmium-plated nickel sheet and a sintered nickel electrode (0.31 mm thick) were employed as the negative substrate electrode and the positive electrode, respectively. The size of the positive and negative electrodes was 2.2 cm × 2.5 cm. The two half-cell electrolytes were separated by a sheet of Nafion 115 cation-exchange membrane to fabricate the electrolysis cell. 35 mL of 0.4 M ZnO in 6 M KOH solution was employed as the cathodic electrolyte and 35 mL propanol of different concentrations in 6 M KOH solution was employed as the anodic electrolyte. Two Xishan pumps (China) were used to pump each half-cell electrolyte through the corresponding half-cell cavity, where the electrolysis reactions occurred. The constant-current electrolysis was carried out at the current density of 20 mA cm⁻² at room temperature. The electrolysis process is controlled by charge time. At the end of electrolysis, the remaining capacity of a sintered nickel electrode was determined by constant-current discharge experiments at room temperature using a three-electrode cell which comprised a sintered nickel electrode charged for 5 h, with a zinc-plated nickel sheet and a Hg/HgO electrode as counter and reference electrodes, respectively. At the same time, the positive nickel electrode was substituted with an air electrode (Boxin Shanghai Battery Corp., China). And then, the air electrode was combined with the zinc electrode in flowing electrolytes to form a discharge cell to deliver the energy stored in the deposited zinc. The discharge process of constant-current was also carried out at the current density of 20 mA cm⁻² at room temperature.

The performance of batteries was evaluated with constant-current charge/discharge experiments by a battery test system CT2000A (Jinnuo Wuhan Corp., China). The battery properties such as the coulombic efficiency, the voltage efficiency and the overall energy efficiency were calculated as that described in the literature [23]. The organic electro-synthesis current efficiency is the ratio of the electrical charge needed theoretically compared to that consumed practically during electrolysis.

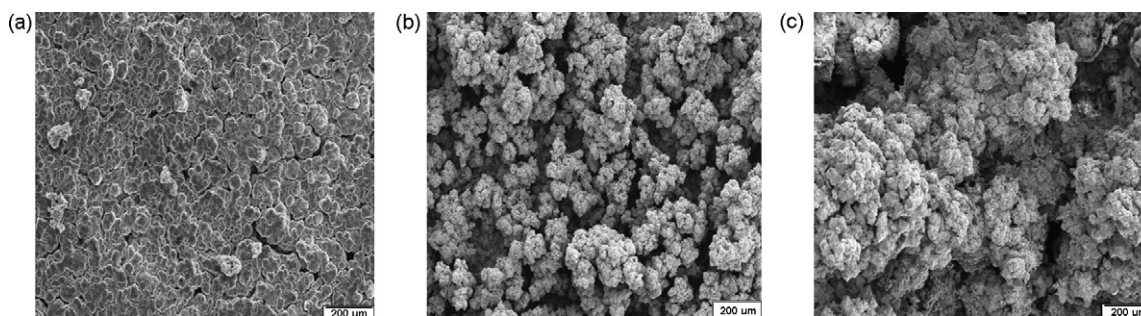
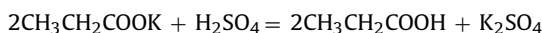


Fig. 2. Surface morphology of the zinc deposited for different times on a cadmium-plated nickel sheet during electrolysis: A, B, and C (charge time 1.5, 3.5, and 5.0 h, respectively).

2.4. Determination of propanoic acid

The propanoic acid prepared electrochemically was determined by a two-step acid–alkali titration method as follows: a sample of 5 mL was removed from the anodic electrolyte at the end of electrolysis. In the strong alkaline solution of KOH, propanoic acid has been converted to potassium propionate. Two drops of the phenolphthalein indicator were added to the sample. And, a 1 M H₂SO₄ solution was used to neutralize the concentrated KOH solution preliminarily. Consecutively, the remaining KOH was titrated with 0.2 M H₂SO₄ until the red solution turned to be colorless. The equation of the neutralization reaction was as follows: 2KOH + H₂SO₄ = K₂SO₄ + 2H₂O. But, the potassium propionate still remained in the solution. And then, two drops of the methyl orange indicator were added into the sample. The sample was titrated with 0.02 M H₂SO₄ until the orange-yellow solution turned to be orange-red. At this time, the volume of 0.02 M H₂SO₄ consumed was recorded as V_s. The reaction equation can be written as



Subsequently, a blank experiment was performed in a similar manner as above except that the sample of 5 mL was removed from the original anodic electrolyte before electrolysis. The volume of 0.02 M H₂SO₄ consumed was recorded as V₀. Hence, the concentration (C) of the electro-synthesized propanoic acid can be calculated by the following equation: $C = 0.02(V_s - V_0)$.

3. Results and discussion

3.1. Effects of zinc deposition behavior

At a certain current density, the amount of deposited zinc is controlled by charge time. The anolyte was 35 mL of 0.1 M propanol in 6 M KOH medium while the catholyte was 35 mL of 0.4 M ZnO in 6 M KOH medium. The effects of changing charge time on the charge/discharge performance of the batteries are listed in Table 1. The 'gas-introducing' cell configuration (see Fig. 1(A)) was employed for discharge.

As seen in Table 1, hardly any difference in the average charging voltage and discharging voltage is observed with an increase in the charge time. They basically keep at the neighborhood of 2.0 V and 1.2 V, respectively. Before the charge time exceeds 5.5 h, the coulombic efficiencies of the batteries are quite high, which are beyond 93%. The energy efficiencies of the batteries are also higher than 53%. The high coulombic efficiency should be attributed to the large hydrogen overpotential on cadmium. When the charge time reaches 7 h, the coulombic and energy efficiencies of the battery exhibit a sharp decline. As a result, the best charge/discharge performance is achieved at the charge time of 5 h. The coulombic

and energy efficiencies of the battery are up to 96.1% and 58.6%, respectively. Correspondingly, the change of the morphology of zinc deposits with charge time was characterized by SEM images as shown in Fig. 2. In all cases, no dendrites are observed over the electrode surface due to flowing electrolytes. A deposit from the charge time of 1.5 h is presented in Fig. 2A. As can be clearly seen, the zinc has deposited as a quantity of compact granular mass. The effects of prolonging the charge time are shown in Fig. 2B and C. With an increase in the charge time, the granular deposits become larger but still relatively dense, which is fairly significant as the charge time is up to 5.0 h. When the charge time is beyond 5 h, the zinc deposits become so thick that the polarization of the zinc electrode could be large. This results in a decrease in the coulombic and energy efficiencies of the battery. Hence, the optimal charge time should be 5 h.

3.2. Effects of discharge cell configuration

Better discharge performance was achieved using the 'cavity-opening' configuration for the discharge cell rather than the 'gas-introducing' configuration, as shown in Fig. 3. A cadmium-plated nickel sheet is used as the negative substrate electrode, the charge time is set as 5.0 h. An increase of about 100 mV in the discharge voltage is found compared to the 'gas-introducing' configuration. From the charge/discharge plot (see Fig. 4), the coulombic and energy efficiency values were calculated as 93.3% and 59.2%, respectively. That means the energy consumed by the propanol oxidation can be recovered by 59.2%. The improvement in discharge performance of the battery is principally attributed to the improved cathode kinetics due to the increased oxidant supply.

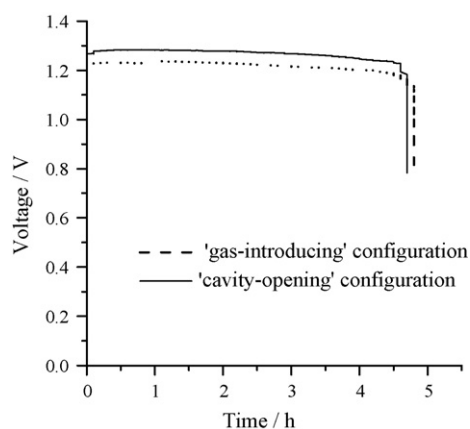
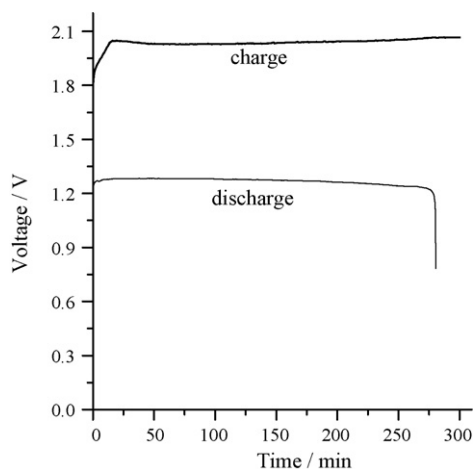


Fig. 3. Effect of discharge cell configurations on discharge curves for test cells. Current density: 20 mA cm⁻².

Table 1Effects of charge time on the charge/discharge performance of the system using a cadmium-plated nickel sheet as the substrate electrode. Current density: 20 mA cm^{-2} .

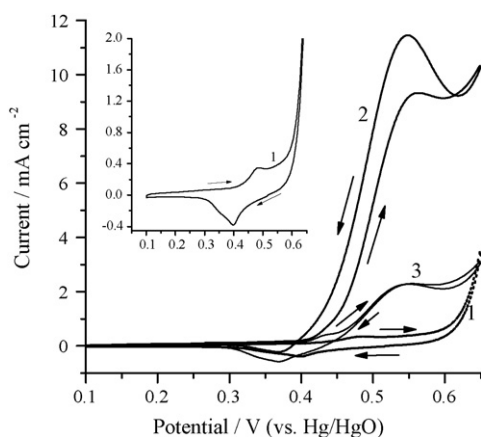
Charge time (h)	Average charge voltage (V)	Average discharge voltage (V)	Coulombic efficiency (%)	Energy efficiency (%)
2.5	2.05	1.14	97.3	54.1
3.5	2.01	1.13	94.7	53.2
4.0	2.00	1.15	95.1	54.7
5.0	2.00	1.22	96.1	58.6
5.5	2.00	1.14	93.0	53.0
7.0	2.06	1.12	88.9	48.3

**Fig. 4.** Charge–discharge curves for this system using the ‘cavity-opening’ cell configuration for discharge. Current density: 20 mA cm^{-2} .

3.3. Organic electro-synthesis on the positive electrode

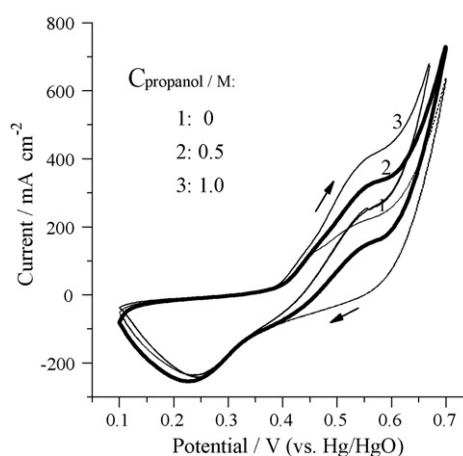
3.3.1. Cyclic voltammogram

Cyclic voltammograms obtained at a scan rate of 10 mV s^{-1} on a nickel electrode for 6 M KOH, 0.5 M propanol and 0.5 M isopropanol in 6 M KOH solutions are shown in Fig. 5. In the inset Fig. 5(1), on the sweep towards positive potentials, a peak is obtained and on the sweep towards negative potentials a similar reverse peak is observed. This anodic peak should correspond to the oxidation of Ni(OH)_2 to NiOOH since nickel placed in contact with a solution of aqueous alkali has been shown to become covered with a layer of nickel hydroxide. From Fig. 5(2) and (3), it can be seen that the addition of propanol or isopropanol converts the anodic peak into a wave. In particular, for the propanol, a significant crossover is observed when scanning the electrode in the negative direction

**Fig. 5.** Cyclic voltammograms recorded at 10 mV s^{-1} on a nickel electrode for various solutions: (1) 6 M KOH, (2) 0.5 M propanol + 6 M KOH, and (3) 0.5 M isopropanol + 6 M KOH.

from 0.65 V. That is, the anodic current density on the reverse scan is conversely higher than that on the positive scan. At the same time, the cathodic peak on the sweep to negative potentials is reduced remarkably. In addition, although the propanol and isopropanol oxidize at the same potential where the higher nickel oxide is produced, the anodic current density of the propanol is much higher than that of the isopropanol. This indicates that the rate controlling step for the reaction between the oxidized nickel surface and the alcohols cannot be an electron transfer process [17]. The reason is that if the rate controlling step was electron transfer, secondary alcohols lose an electron much more readily than primary alcohols. Therefore, the propanol oxidation at a nickel electrode should be a catalytic oxidation process by electrochemically generated NiOOH [17,18].

Cyclic voltammograms obtained at a scan rate of 5 mV s^{-1} on a sintered nickel electrode in 6 M KOH solutions containing propanol of various concentrations are shown in Fig. 6. In Fig. 6(1), an anodic peak is observed at a potential of around 0.54 V indicating the Ni(II) is oxidized to Ni(III) , while the corresponding cathodic peak appears at approximately 0.25 V. Fig. 6(2) and (3) shows that in 6 M KOH solution containing propanol of various concentrations, the current density value is always positive either on the positive scan or on the reverse scan in the potential region of 0.40–0.60 V, and the current density increases with the increase of propanol concentration. The reason is that with the increase of propanol concentration, the amount of Ni(II) produced by reduction of Ni(III) through the chemical reaction with propanol is enhanced, leading to a rise in the anodic current density of Ni(II) . Moreover, by comparison with Fig. 5, in all cases, the current density at a sintered nickel electrode is much higher than that at a nickel electrode. This indicates that a sintered nickel electrode exhibits much better catalytic activity for the propanol oxidation than a nickel electrode. On the other hand, the cathodic peaks of the three voltammograms at the potential of 0.25 V in Fig. 6 are almost overlapped. This suggests that the chemical reaction speed for the propanol oxidation is slower than that for the electro-oxidation of Ni(II) . Thus, the anodic current density

**Fig. 6.** Cyclic voltammograms recorded at 5 mV s^{-1} on a sintered nickel electrode for 6 M KOH solution containing propanol of different concentrations.

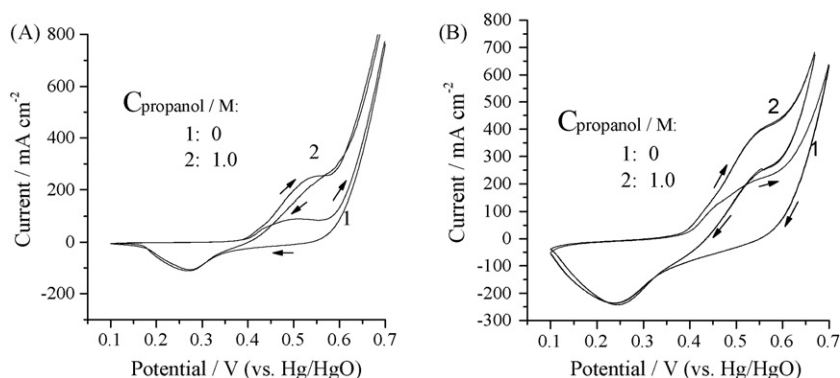


Fig. 7. Cyclic voltammograms recorded at 1 mV s^{-1} (A) and 5 mV s^{-1} (B) on a sintered nickel electrode for 6 M KOH solution and 1 M propanol in 6 M KOH solution, respectively.

is not raised considerably with the increase of propanol concentration. There are still a certain amount of unreduced Ni(III) remained on the electrode. The voltammograms show an almost unchanged cathodic peak even in 6 M KOH solution containing propanol during the negative scan.

In order to illuminate the relationship between the scan rate and the reaction speed for the propanol oxidation further, comparison of the voltammograms recorded at different scan rates on a sintered nickel electrode in 6 M KOH solution and 6 M KOH solution containing 1 M propanol is given in Fig. 7. It can be seen that when the scan rate is decreased from 5 mV s^{-1} to 1 mV s^{-1} , the anodic current density is increased more substantially owing to the addition of propanol. In addition, a crossover in cyclic voltammogram occurs when scanning the electrode in the negative direction from 0.70 V. This is due to the fact that the concentration of intermediates produced by the oxidation propanol at the electrode surface during the positive scan is so large that they cannot be oxidized completely. In this case, the anodic current density on the reverse scan is higher than that on the positive scan. This indicates that when the scan rate is reduced, a difference between the electro-oxidation speed of sintered nickel electrodes and the catalytic oxidation speed of propanol is shortened. As a result, the electro-catalysis function of a sintered nickel electrode for the propanol oxidation is displayed more remarkably.

3.3.2. Effects of propanol concentrations

It is shown from the cyclic voltammograms that in the propanol oxidation, the propanol concentration plays an important role. In order to explore the relation between the organic electro-synthesis and propanol concentration, effects of changing the propanol concentration on the charge performance of batteries and the organic electro-synthesis efficiency were investigated. The catholyte was 35 mL of 0.4 M ZnO in 6 M KOH medium while the anolyte was 35 mL of propanol of different concentrations in 6 M KOH medium. According to the above results, the batteries were electrolyzed for 5 h at the current density of 20 mA cm^{-2} , using a cadmium-plated nickel sheet as the negative substrate electrode. The results are listed in Table 2. From the results of cyclic voltammograms, it is

found that, at the end of electrolysis, there should be a certain amount of unreduced Ni(III) remained on the sintered nickel electrode. To further demonstrate this result, the remaining capacity of a sintered nickel electrode was determined using a three-electrode cell. Variation of the remaining capacity of a sintered nickel electrode with the concentration of propanol is also listed in Table 2. When propanol is not contained in the anolyte, the charged sintered nickel electrode can yield a discharge capacity of 105 mAh. As seen from Table 2, the addition of propanol leads to a distinct decline in the discharge capacity yielded by a charged sintered nickel electrode. Also, this discharge capacity is reduced gradually from 67 mAh to 45 mAh with the increase of the propanol concentration. This is in agreement with the results of cyclic voltammograms. The remaining capacity should result from a certain amount of unreduced Ni(III) remained on the sintered nickel electrode. In view of the anolyte needed to be removed immediately at the end of charge, it is impossible to ensure that the remaining NiOOH can react continuously with the propanol. It indicates that within the error range, the determination of the propanoic acid concentration should be quantitative on this condition.

As can be seen from Table 2, with increasing the concentration of propanol, the concentration of the electro-synthesized propanoic acid is raised gradually as well as the organic electro-synthesis current efficiency. This is particularly significant as the concentration of propanol is increased to 0.5 M. However, when the propanol concentration is increased further, only a little rise in the concentration of propanoic acid is observed. When the concentration of propanol is as high as 1.0 M, the organic electro-synthesis current efficiency is up to 82%. This suggests that there still exists the side reaction of oxygen evolution on the anode because of the slow oxidation rate of propanol. But, the higher the concentration of propanol, the less is the effect of oxygen evolution on the propanol oxidation. Thus, the efficiency is enhanced with the increase of the propanol concentration.

In addition, a preferential transfer of water from the anodic to the cathodic half-cells is observed, the rate of which is not dependent on the concentration of propanol. Moreover, the amount of water transfer is rather small that it is only about 1 mL. This is mainly

Table 2
Effects of the propanol concentration on the charge performance of the system and the organic electro-synthesis efficiency.

Propanol concentration (M)	Water transfer ^a (mL)	Average charge voltage (V)	Propanoic acid concentration (M)	Remaining capacity of sintered nickel electrodes (mAh)	Organic electro-synthesis current efficiency (%)
0.15	1.0	1.98	0.04	67	27
0.30	0.9	1.98	0.06	65	41
0.50	1.0	1.84	0.10	56	68
0.70	0.8	2.02	0.09	57	61
1.00	1.0	1.82	0.12	45	82

^a Expressed by the decrease in the volume of the anolyte.

due to the fact that the concentrated KOH solution is used as the supporting electrolyte in both the anolyte and the catholyte. Further, zincate ions in the catholyte are deposited continuously on the substrate electrode during electrolysis. On the other hand, organic molecules in the anolyte are large and their concentration is relatively low. In the strong alkaline solution, the product, propanoic acid, exists in the form of a weak alkali, namely, $\text{CH}_3\text{CH}_2\text{COOK}$. Anion ions are restricted in permeating across the cation-exchange membrane. As a result, water transfer between the anolyte and the catholyte is principally dependent on the supporting electrolyte. Similarly, no change is observed in the average charge voltage of the cell with the increase of the propanol concentration, keeping a stable value of around 1.9V. During electrolysis, in essence the synthesis of propanoic acid is an indirect electro-oxidation from propanol by oxidation with electrochemically generated NiOOH on the sintered nickel electrode. Thus, the propanol concentration in the anolyte does not influence the charge voltage.

4. Conclusion

From the results obtained in the present work, the following conclusions can be drawn:

- (1) A cadmium-plated nickel sheet is used as the substrate electrode. The dendritic growth and hydrogen evolution are prevented effectively. Granular zinc deposits become larger but still relatively dense with increasing the charge time. The battery still exhibits a favorable charge/discharge performance even if the charge time is as long as 5 h at the current density of 20 mA cm^{-2} .
- (2) When the discharge cell configuration changes from 'gas-introducing' into 'cavity-opening', an increase of about 100 mV in the discharge voltage is obtained due to the improved cathode kinetics resulting from the increased oxidant supply. The energy efficiency of the battery is up to 59.2%. That means, the energy consumed by the organic electro-synthesis can be recovered by 59.2%.
- (3) The sintered nickel electrode exhibits a good electro-catalysis activity for the propanol oxidation. The increase of propanol concentration conduces to an enhancement in the organic

electro-synthesis efficiency. When the propanol concentration is up to 1 M, the highest organic electro-synthesis current efficiency of 82% is achieved. In addition, water transfer between the anolyte and catholyte is quite low. Also, the water transfer and charge voltage basically have no relationship with the propanol concentration.

- (4) It is demonstrated that the principle of a zinc-air battery using zinc regeneration electrolysis with propanol oxidation as a counter electrode reaction is feasible.

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