

Nanostructured silver catalyzed nickel foam cathode for an aluminum–hydrogen peroxide fuel cell

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Abstract

A nanostructured Ag catalyzed nickel foam cathode for an aluminum–hydrogen peroxide fuel cell was prepared using an electrodeposition technique. SEM images show that Ag nano-islands, about 2–3 μm in length and 100–200 nm in width are aligned on the surface of the Ni foam substrate. The composition of the catalyst layer of the cathode was examined by XRD. Electrochemical performance and stability of the cathode for the reduction of hydrogen peroxide in aluminum–hydrogen peroxide fuel cell were studied.

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1. Introduction

The aluminum–hydrogen peroxide ($\text{Al-H}_2\text{O}_2$) fuel cell has received considerable attention due to its high energy density, high power density and long duration. The system with hydrogen peroxide, as an alternative source of oxygen, is of special interest for underwater applications. The aluminum–hydrogen peroxide fuel cell using H_2O_2 as the cathodic reactant was studied extensively by Dow et al. [1].

The conductivity and porosity of the cathode are of significant importance for the reduction reaction of hydrogen peroxide. High electronic conductivity can ensure effective collection of the current and reduce ohmic resistance. Poor mass transport of reactants (e.g. hydrogen peroxide) or products, which can be caused by low electrode porosity, and can significantly increase polarization and thereby reduce the operating voltage. The catalytic activity of the electrode also plays an important role in the reduction reaction of hydrogen peroxide. One method to reduce the polarization of the electrode is to increase the number of active sites on the catalyst. For this purpose, a variety of electrocatalytic cathodes for reduction of hydrogen peroxide have been investigated in recent years [2,3].

Hasvold et al. [4] studied the use of large “bottle brush” catalyzed carbon fiber electrodes in a non-separated $\text{Al-H}_2\text{O}_2$ system at the 5 mM level of H_2O_2 . Their success was attributed to an increase in the ratio of cathode to anode active area. Bessette et al. [5,6] fabricated a microfiber carbon electrode (MCE) using a textile science flocking technique. Carbon fibers are aligned perpendicular to the surface of a conductive carbon epoxy coated carbon paper substrate. MCE covered with Pd/Ir catalyst can increase specific surface area and improve the mass transport of reactant.

This paper presents a high performance cathode via a surface modification of a porous Ni foam substrate for an aluminum–hydrogen peroxide fuel cell. Characterization of the morphology and structure of the Ag deposit layer was carried out using SEM and XRD analysis. Fuel cell tests were also conducted to examine the catalytic activity and stability of the nano-structured silver catalyzed Ni foam cathode.

2. Experimental

2.1. Preparation of the electrode

All chemicals used in this investigation were of reagent-grade quality and used as obtained from the supplier (J&K Chemical

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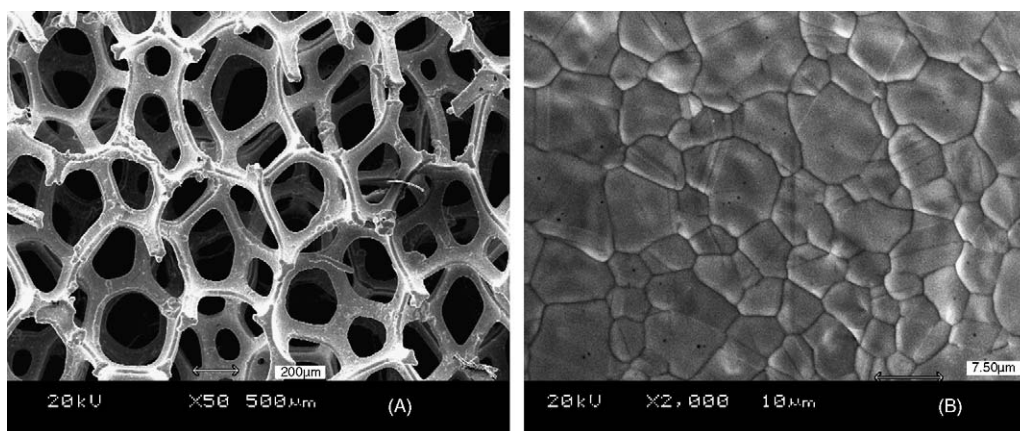


Fig. 1. SEM image of the Ni foam. (A) Ni foam and (B) Ni foam surface.

Ltd.) without further purification. All solutions were prepared using deionised water.

The metal substrate used in this work was Ni foam (thickness: 1.0 mm, pore density: 110 ppi, from Shenzhen Rolinsia Power Materials Ltd.). An SEM image of the Ni foam is shown in Fig. 1. Foamed nickel has a three-dimensional grid structure and shows a high porosity and a high specific surface area, with considerable and uniform strength and tenacity.

To clean and etch the metal surface, acetone and hydrochloric acid were employed. Ni foam substrates were immersed in acetone to remove grease from the surfaces, and then dried in air. After this process, Ni foam substrates were immersed in 3 M HCl at 25 °C for 20 min to remove the oxide layer and etch the Ni foam surface. After preparation, the Ni foam substrates were rinsed with deionised water to remove chemicals prior to further use.

The silver catalyst can be prepared via direct current electrodeposition onto the foamed nickel substrate, by controlling the electrolyte system composition and deposition conditions. The solution used for the deposition contained 50 g l^{-1} of $\text{KAg}(\text{CN})_2$. Electrodeposition was carried out at a current density of 5 mA cm^{-2} at room temperature. The electrodeposition time was controlled to obtain a coating thickness of about $1 \mu\text{m}$. After deposition, a gray metal silver film was formed on the fiber wall of porous Ni foam substrate.

2.2. Analysis of electrode

The surface morphology of the Ni foam substrate and the metallic silver catalyst deposited on the Ni foam substrate were characterized by employing a JEOL JSM-5600LV scanning electron microscope.

The linear polarization analyses were carried out using an EG&G 273A electrochemical system. A three-electrode system was used for electrochemical analysis. The electrolyte was 2.0 M NaOH, 0.5 M H_2O_2 and 40 g l^{-1} NaCl solution. A catalyzed substrate cathode was used as a working electrode, a Ag/AgCl electrode as a reference electrode, and a Pt foil used as a counter electrode. The scan rate was set at 1 mV s^{-1} at a range of 0 to -1.5 V (versus Ag/AgCl).

Fuel cell performance was carried out using a flow through test cell ($30 \text{ mm} \times 50 \text{ mm}$) made of plexiglass. The electrode area was 2.0 cm^2 ($10 \text{ mm} \times 20 \text{ mm}$). The cell gap between two electrodes was maintained at 1.0 mm. The two electrodes were mounted vertically and were separated by a plastic grid. The electrolyte was pumped into the bottom of the cell, flowed between the anode and the cathode surface and exited at the top of the cell. The fuel cell was incorporated into a closed-loop flowing electrolyte apparatus consisting of a heated electrolyte reservoir, a peristaltic pump and a heat exchanging coil in a constant temperature bath. The performance of Al- H_2O_2 fuel cell was recorded by the computer data logging system (Arbin system).

3. Results and discussion

3.1. Characterization of electrode surface

The surface morphology of the cathode was observed with a scanning electron microscope (SEM) as shown in Fig. 2. It can be seen that the gray silver coating is a uniform film with a fiber structure and adheres firmly to the Ni substrate.

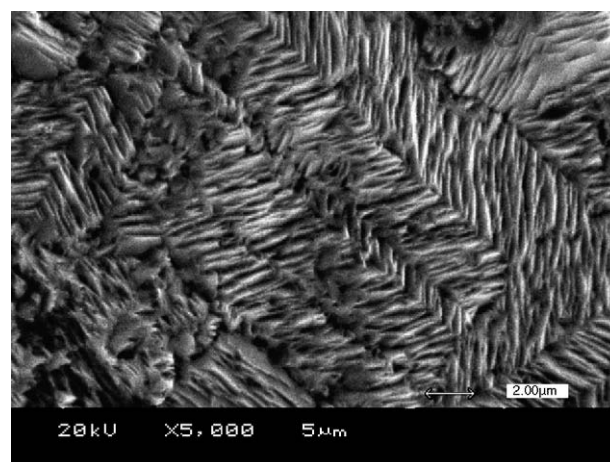


Fig. 2. SEM image of the Ag catalyzed Ni foam electrode.

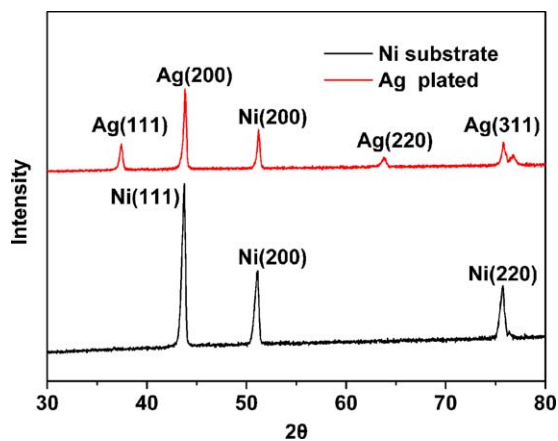


Fig. 3. XRD patterns of Ni foam and Ag catalyzed Ni foam electrode.

The fibrous nano-islands, 2–3 μm long and 100–200 nm wide, were aligned on the fiber wall of the porous nickel foam substrate. It is evident that an increase in specific catalytic surface area of several times occurs with the application of the nano-structured Ag catalyzed Ni foam cathode. BET characterization of the total surface area ascertained the increase in surface area with formation of the catalyst clusters. For the electrochemically deposited silver catalyst, the total volumetric surface area will be several times – 428 cm^2 per cm^3 – of electrode volume.

Fig. 3 shows the X-ray diffractograms in the 2θ range 30–80° of the Ni substrate deposited with Ag. For Ni substrate deposited with Ag catalyst, the diffraction peaks corresponding to Ni are observed. The composition of the deposit analyzed by XRD showed that the content of the deposit is mostly Ag with a trace of Ni.

3.2. Electrode performance test under various conditions

3.2.1. Effect of temperature

Fig. 4 shows the electrode polarization curves performed at 10, 20, 30, 40 and 50 °C. It is clearly shown that the electrode performance improved as the temperature increased. The polarization curves shifted to more positive potential as the tem-

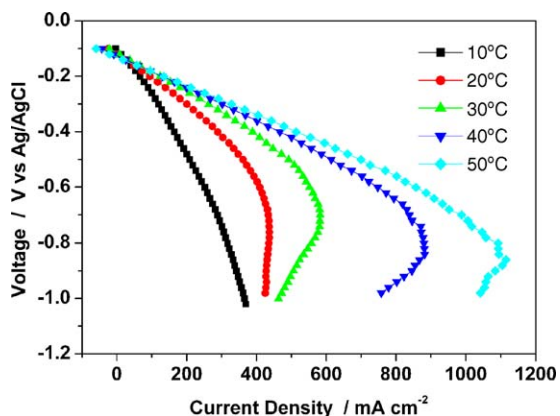


Fig. 4. Temperature effects on electrode performance. Test operated at 10, 20, 30, 40 and 50 °C. Electrolyte: 0.5 M H_2O_2 , 2 M NaOH and 40 g l^{-1} NaCl.

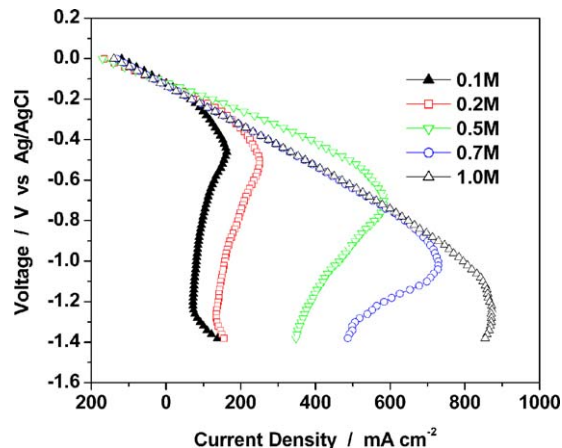


Fig. 5. Effects of H_2O_2 concentration on electrode performance. Temperature: 30 °C; electrolyte: 2 M NaOH, 40 g l^{-1} NaCl with H_2O_2 concentrations of 0.1, 0.2, 0.5, 0.7 and 1.0 M.

perature increased. This behavior confirms that the hydrogen peroxide reduction was better at a higher temperature.

3.2.2. Effect of hydrogen peroxide concentration

As a high reaction activity is generally desirable, a higher concentration of hydrogen peroxide is preferred in use. However, The decomposition reaction of hydrogen peroxide is more significant at high concentration of H_2O_2 . To investigate the effect of hydrogen peroxide concentration on the electrode performance, 0.1, 0.2, 0.5, 0.7 and 1.0 M hydrogen peroxide were used and the electrode polarization curves are shown in Fig. 5. With the concentration of H_2O_2 increase, the electrode performance increased generally. However, when the concentration of H_2O_2 increased to above 0.7 M, the decomposition reaction is severe. This decomposition within the cell generates gas bubbles, which can reduce the effective electrode surface area. As a result, the electrode performance degraded as the concentration of hydrogen peroxide exceeded 0.5 M. The best electrode performance was obtained using 0.5 M hydrogen peroxide.

3.2.3. Effect of NaOH concentration

Fig. 6 is a graph of the cathodic polarization curves for sodium hydroxide concentrations of 0.5, 1.0, 2.0 and 3.0 M. It is noticed that the higher electrolyte concentration gives a better electrode performance. An explanation for this could be attributed to the increase of electrolyte conductivity, which can lower the resistance of the electrolyte and thus can affect electrode performance. This would lead one to increase the NaOH concentration further. However, fuel cell tests showed that, above 2.0 M NaOH, a very large amount gas was produced in the cell. This gas is most likely due to the aluminum corrosion reaction, which produces hydrogen, and the enhanced decomposing of hydrogen peroxide occurs with higher NaOH concentration.

3.2.4. Comparison of different electrodes

A comparison of the catalytic performance of different catalysts for the reduction of H_2O_2 in a sodium hydroxide–sodium chloride electrolyte at 55 °C is presented in Fig. 7. The superior

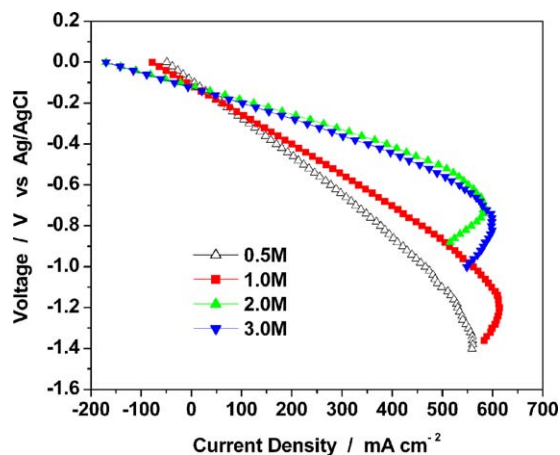


Fig. 6. Effects of NaOH concentration on electrode performance. Temperature: 30 °C; electrolyte: 0.5 M H₂O₂, 40 g l⁻¹ NaCl with NaOH concentrations of 0.5, 1.0, 2.0 and 3.0 M.

performance of the electrocatalytic cathode prepared by electrodeposition of the Ag catalyst onto a Ni foam substrate over the entire current density range is clearly evident. The maximum cathodic polarizing current density reached to 1300 mA cm⁻² at -1.0 V (versus Ag/AgCl) in electrolyte solution which contained 0.5 M H₂O₂, 2.0 M NaOH and 40 g l⁻¹ NaCl at 55 °C.

The potential advantages of applying catalyzed metal substrates are the high catalytic activity, and also reduction of diffusion resistance by direct contact between the electrolyte, hydrogen peroxide, and the catalyst.

The polarization curve 3 of a Ni foam baseline catalyst is included for comparison, which shows that metallic nickel is not catalytically active for the reduction of hydrogen peroxide.

3.2.5. Short-term stability test

Fig. 8 shows a durability test of 125 h under constant load of 400 mA cm⁻² at 40 °C for Ag catalytic electrodes. The electrolyte solution contains 0.5 M H₂O₂, 2.0 M NaOH and 40 g l⁻¹ NaCl. The electrolyte was replaced every about 10 h. It is seen that the electrode showed an excellent stability over the entire test duration of 125 h under constant load of 400 mA cm⁻² at 40 °C.

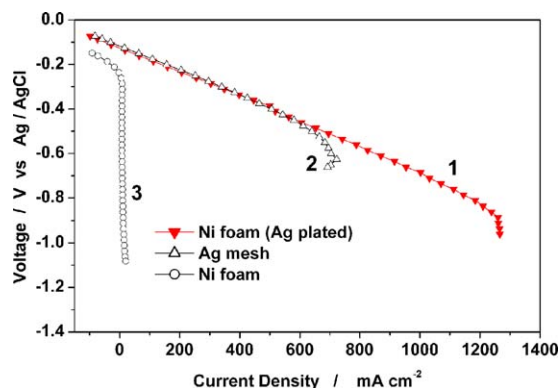


Fig. 7. Cathodic polarization curves for different electrodes at 55 °C. Electrolyte: 0.5 M H₂O₂, 2.0 M NaOH and 40 g l⁻¹ NaCl.

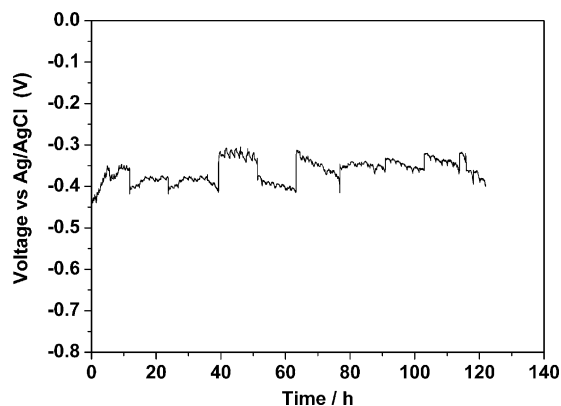


Fig. 8. Stability test of the Ag catalyzed Ni foam electrode. Temperature: 40 °C; constant load current density: 400 mA cm⁻²; electrolyte: 0.5 M H₂O₂, 2.0 M NaOH and 40 g l⁻¹ NaCl.

3.3. Fuel cell performance tests

The discharge curves of Al-H₂O₂ fuel cell using different cathodes were showed in Fig. 9. The electrolyte solution contains 0.5 M H₂O₂, 2.0 M NaOH and 40 g l⁻¹ NaCl. The operation temperature is 45 °C. The improved performance of the Al-H₂O₂ cell incorporating Ag catalyzed Ni foam is clearly evident. Cell voltage measured at 250 mA cm⁻² for the Al-H₂O₂ fuel cell containing Ag catalyzed cathode was as much as 500 mV higher than that of planar Ag mesh. The peak power density of an Al-H₂O₂ single cell reached to 450 mW cm⁻².

Fig. 10 shows the cell performance curves for tests performed at lower temperatures (e.g. 10, 20 and 30 °C). The electrolyte solution contained 0.5 M H₂O₂, 2.0 M NaOH and 40 g l⁻¹ NaCl. It is shown that the cell performance improved as the temperature increased. The higher temperature gave a higher open circuit voltage and a higher power density.

The improved cell performance might be due to unique structure of the cathode. The open porous and interconnected structure of the Ni foam substrate enables the liquid reactant easily reach the surface of the catalyst, thus reduce the mass transport resistance of the reactant significantly. The highly dispersed

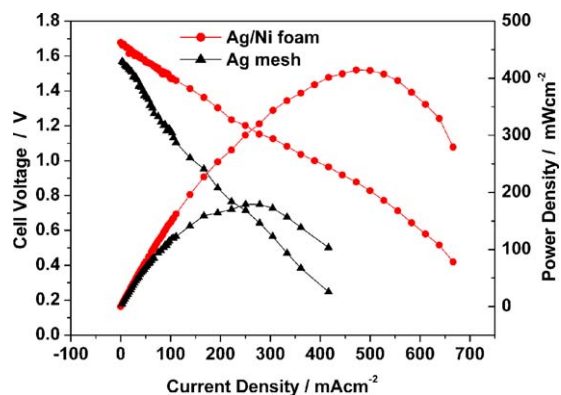


Fig. 9. Performance comparison of Al-H₂O₂ fuel cells with different cathodes at 45 °C. Anode: 99.996% aluminum; electrolyte: 0.5 M H₂O₂, 2.0 M NaOH and 40 g l⁻¹ NaCl.

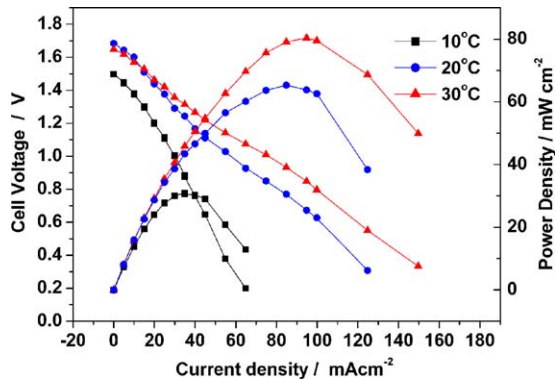


Fig. 10. Effects of temperature on fuel cell performance at lower temperature. Cell operated at 10, 20 and 30 °C; anode: 99.996% aluminum; cathode: Ag catalyzed Ni foam cathode; electrolyte: 2 M NaOH, 0.5 M H₂O₂ and 40 g l⁻¹ NaCl.

nano-island-like structure of the Ag deposit layer extends the active surface area of the Ag catalyst.

4. Conclusions

An Al–H₂O₂ fuel cell cathode using Ag catalyzed Ni foam produced by electrodeposition of metallic Ag catalyst, was successfully prepared. A highly dispersed Ag deposit with a porous nano-island like structure and a highly active surface area was obtained. Surface properties and morphology of the

Ag deposit on Ni foam were characterized using SEM and XRD analysis.

The nanostructured silver catalyzed Ni foam cathode showed high catalytic activity and gave stable electrode performance. The electrode provides a high surface area in the catalyst layer and offers lower mass transport resistance, which is suitable for the application of Al–H₂O₂ fuel cell.

Acknowledgements

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