

Studies of a granular aluminum anode in an alkaline fuel cell

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Abstract

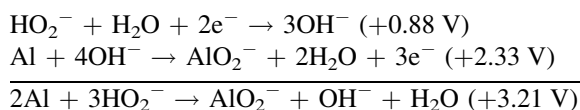
A granular aluminum anode was investigated for use in an alkaline aluminum/hydrogen peroxide fuel cell. The fuel cell utilizes granules of aluminum (8–12 mm in diameter) as an anode, potassium hydroxide (KOH) as an anolyte and hydrogen peroxide as a catholyte. Granular anodes have a significantly higher surface area than planar surfaces, thereby resulting in higher utilization of the anode material. Polarization experiments were performed as well as closed circuit power production experiments. KOH concentrations were varied in the experiments. Polarization experiments achieved a current density of 10.02 mA/cm² using 2 M KOH and granular aluminum with a surface area of 205.6 cm². Power production experiments sustained a current density of 0.05 mA/cm² using 1.5 M KOH and granular aluminum with a surface area of 59.8 cm². Results indicate that granular metal anodes have potential for use in high energy density fuel cells.

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Keywords: Alkaline fuel cell; Particulate anode; Surface area; Aluminum; Hydrogen peroxide

1. Introduction

The use of fuel cells as environmentally friendly power sources is of increasing interest. Alkaline fuel cells have been investigated for use in automobiles and unmanned underwater vehicular [1–4]. Fuel cells that have been studied for vehicular applications contain plate-type metal anodes (aluminum and magnesium), potassium hydroxide (KOH) anolytes (combination of metal anode and electrolyte) and hydrogen peroxide catholytes (combination of cathodic oxidizer and electrolyte). This type of fuel cell is attractive for these applications due to a relatively high faradic capacity and a high standard potential [5]. For the aluminum/hydrogen peroxide system, the equations half-cell with respect to the standard hydrogen electrode are:



As indicated by Dow et al., hydrogen peroxide is deprotonated in highly alkaline solutions yielding the HO₂[−] representation [6]. With improvements to performance of alkaline fuel cells, it is hoped that they will be able to be utilized for other small electronic devices.

Many different variables in metal/hydrogen peroxide fuel cells have been investigated to improve fuel cell performance. Half-cell membrane separators have been used to improve fuel cell performance by limiting direct non-electrochemical reactions [7]. Palladium and iridium catalysts have been investigated to improve cell efficiency through their promotion of the cathodic decomposition of hydrogen peroxide, noted in the half-cell equations [8]. Protective films that deposit on aluminum anodes and decrease cell current have been removed by use of electrolyte additives [9,10]. Additives such as citrate, tartrate, indium and gallium have proven to inhibit aluminum corrosion, thus, increasing the galvanic activity of the cell.

Increasing cathodic surface area of alkaline fuel cells has led to improvement in cell performance. Bessette et al. have developed a cathode with high surface area through the application of small, catalyzed carbon fibers to a carbon epoxy coated carbon paper [11]. Through the increased cathode surface area, it was suggested by Bessette that lower concentrations of hydrogen peroxide could produce cell voltages that compete with the relatively high hydrogen peroxide concentrations previously utilized.

The objective of this paper is to present data on an alkaline fuel cell that contains aluminum granules as its primary anode. The use of a granular aluminum anode is advantageous due to the high anode surface area that it creates. The higher surface area achieved by a particulate anode will allow more aluminum to react, thus, increasing cell output.

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Polarization experiments as well as power production experiments will be presented in this paper.

2. Experimental

The fuel cell apparatus used was a machined piece of Plexiglas, measuring 3.5 in. \times 3.5 in. The cell consisted of two half-cells with internal reaction chambers (Fig. 1). A 0.25 in. thick piece of Plexiglas with twenty, 1 mm in diameter holes separated the two reaction chambers. A 0.01 in. thick

piece of stainless steel (Alfa Aesar 41584) served as the current collector in each reaction chamber. Aluminum granules (Alfa Aesar 10093, 99.9% metal basis), 8–12 mm in diameter, served as the particulate anode (Fig. 2). A port for measuring gas evolution was installed on the anode portion of the half-cell. A recycle system was used for the fuel cell reactants. In the recycle system, two, 2 l glass vessels were utilized. One vessel contained a 20% hydrogen peroxide (Fisher H325) catholyte and the other contained the KOH (Fisher P246) anolyte. Cole Parmer peristaltic pumps (7553-80) were used to pump the reactants into and out of the cell in the flow loop set-up.

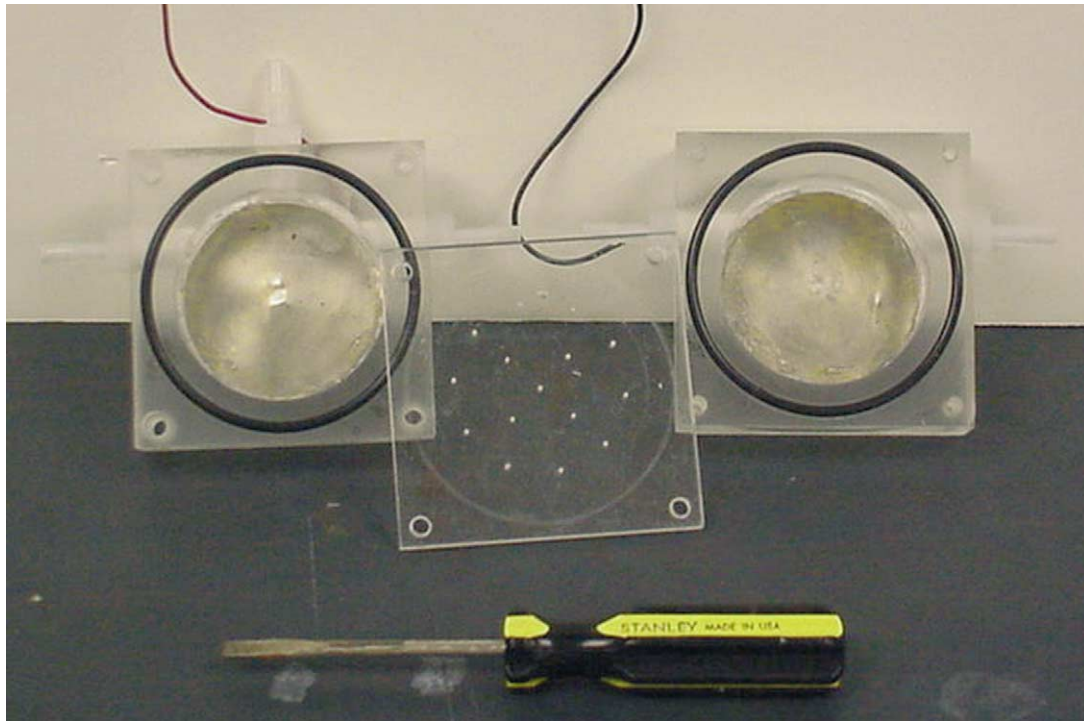


Fig. 1. Fuel cell apparatus with exterior dimensions of 3.5 in. \times 3.5 in.



Fig. 2. Granular aluminum anode, 8–12 mm in diameter, 99.9% purity.

The surface area of the aluminum spheres was determined by a reaction shell balance equation. Hydrochloric acid (Pharmco 284000) was passed through a packed column containing the 8–12 mm aluminum granule anodes. The concentration of the aluminum exiting the packed column was measured with a Thermo Jarrell ash-inductive coupled plasma-atomic emissions spectroscopy. The measured aluminum concentration was placed into the shell balance equation to determine the aluminum surface area.

For the applied potential versus current density investigation of the particulate aluminum anode, a Sorensen model LH 18-20 dc power supply was used to control the power supplied. The experiments used a three-electrode set-up consisting of: a silver/silver chloride reference electrode, granular aluminum working electrode and a stainless steel auxiliary electrode. An Omega mass flow meter (FMA 1700/1800) was used to measure gas production. Cell input and output temperatures were measured using Omega thermocouples. Gas evolution and input and output temperatures were recorded using LabTech notebook software. Fuel cell performance in both the potential versus current density investigation as well as the power production investigation was monitored using LabTech notebook.

3. Results and discussion

The results presented in the following sections are for polarization and power production experiments.

3.1. Polarization investigation

Polarization profiles were prepared for the granular aluminum anode and are presented in Fig. 3. The current density was investigated by applying voltages ranging from 0 to 1 V dc versus the Ag/AgCl reference electrode. The current density was calculated by dividing the current

obtained by the surface area of the granular aluminum anode. For the 1 M KOH polarization profile, the surface area of the granular aluminum anode was 215.1 cm². The surface area of the granular aluminum anode in the 2 M KOH concentration profile was 205.6 cm². The concentration of the KOH anolyte was varied to investigate its effects on the current density of the granular aluminum anode. An amount of 1.0 and 2.0 M KOH were used in the experiments. The flow rate of the anolyte and catholyte was 63 ml/min. The catholyte and anolyte were kept at room temperature, 22 °C.

Higher current density outputs were observed using 2 M KOH anolyte concentrations versus the 1 M KOH anolyte concentrations, Fig. 3. As indicated in Fig. 3, at an applied potential of 1 V dc, the current density achieved by the 2 M KOH anolyte is approximately 10.02 mA/cm². For the same applied potential, the 1 M KOH anolyte achieves approximately 2.98 mA/cm². It should be noted that in all experiments performed, an AlOH layer formed on the granular aluminum anode. The sharper initial rise in the 2 M KOH polarization profile is attributed to the higher electrolyte concentration underlying the higher anolyte concentration. Anolyte concentrations above 2 M KOH were investigated. However, concentration above 2 M KOH caused the fuel cell reaction to become uncontrollable. Thus, for the polarization experiments described, the 2 M KOH concentrations displayed more favorable current density outputs than the 1 M KOH anolyte concentrations.

3.2. Power production

Power production experiments were performed in a closed circuit set-up to view fuel cell performance when its reactions were not being controlled by a supplied potential. Currents density versus time is displayed in Fig. 4. In each experiment performed, granular aluminum anode with a surface area of 59.8 cm² was used. The cell

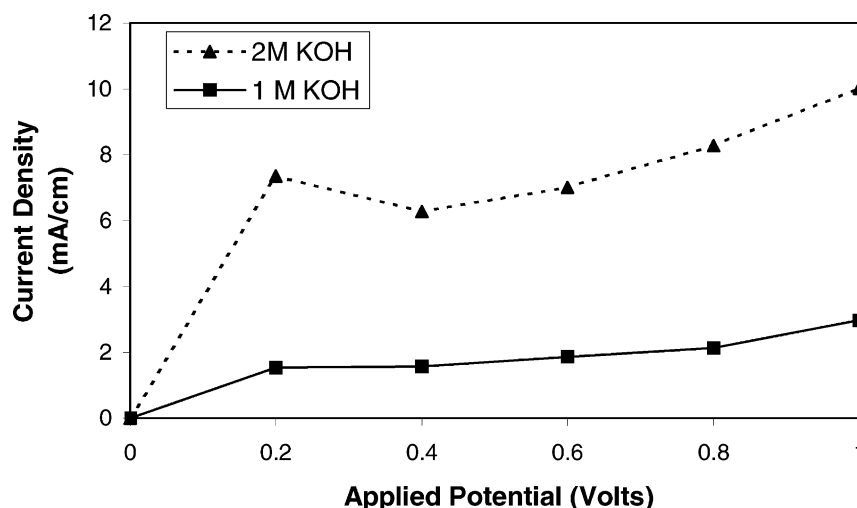


Fig. 3. Current density produced with 1.0 and 2.0 M KOH anolyte concentrations at various applied potentials.

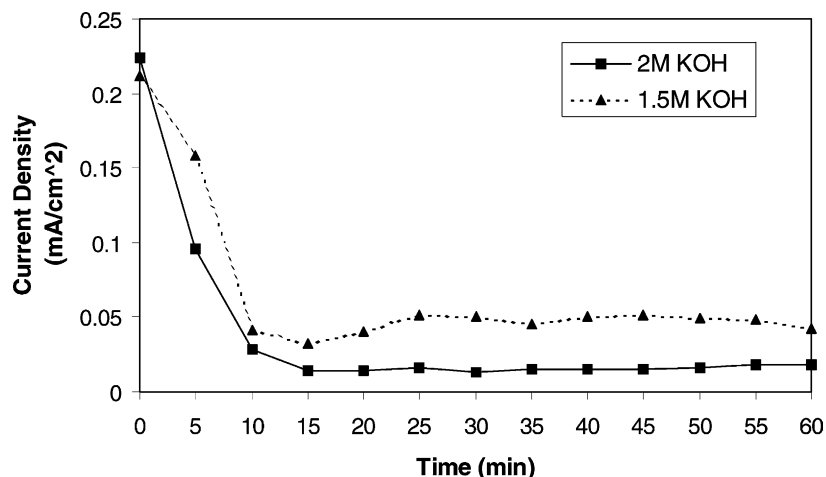


Fig. 4. Current density vs. time for power production at 1.0 and 2.0 M KOH anolyte concentrations.

was in operation for 60 min. The catholyte and anolyte were kept at room temperature and a flow rate of 110 ml/min. Similar to the polarization experiments, concentration of the KOH anolyte was varied to investigate its effects on the current density versus time experiments on the granular aluminum anode. 1.5 and 2.0 M KOH were used in the experiments.

Higher current densities were sustained over time using the 1.5 M KOH anolyte concentrations, Fig. 4. The sharp initial decline in current density is attributed to an AlOH layer that forms on the granular aluminum anode material. The sharper initial decline in current density for the 2 M KOH anolyte concentrations indicates that the AlOH diffusional layer is thicker than the layer formed from the 1.5 M KOH anolyte concentrations. In these open circuit power production runs, the formation of the AlOH layer greatly inhibits the diffusion of the aluminum ions to the bulk anolyte solution. After the initial decline in current density, the anolyte solution containing the 1.5 M KOH sustained a current density of approximately 0.05 mA/cm². The anolyte containing the 2.0 M KOH, however, sustained a current density of only approximately 0.015 mA/cm². Thus, for power production experiments not driven by applied potential, the 1.5 M KOH anolyte displays better sustained current density results over time. Previous research techniques involving electrolyte additives and small concentrations of acids could be utilized to combat the formation of the current inhibiting corrosion layers [2,9,10].

Aluminum/hydrogen peroxide fuel cells have the capacity to generate more than 20 times the power per pound compared with traditional car batteries. Based on the results presented in this paper, and using higher concentrations of hydrogen peroxide (exceeding 70%), granular electrode aluminum/hydrogen peroxide fuel cells can produce specific energies of about 200 Wh/lb m, producing 1.5 V at current densities of 40 mA/cm².

4. Conclusions

The use of a granular aluminum anode has been proven in an alkaline aluminum/hydrogen peroxide fuel cell. Polarization experiments performed using 2 M KOH as an anolyte and a granular aluminum anode with a 205.6 cm² surface area displayed current densities of 10.02 mA/cm² at 1 V dc. Closed circuit power production experiments utilizing 1.5 M KOH and an aluminum anode with a surface area of 59.8 cm² has shown sustainable current densities of approximately 0.05 mA/cm². Upon further system modifications and stacking technology, a granular metal anode has potential for use in a high energy density fuel cell.

Acknowledgements

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References

- [1] O. Hasvold et al., The alkaline aluminum/hydrogen peroxide power source in the Hugin II unmanned underwater vehicle, *J. Power Sources* 80 (1999) 254–260.
- [2] M.G. Medeiros, E.G. Dow, Magnesium-solution phase catholyte seawater electrochemical system, *J. Power Sources* 80 (1999) 78–82.
- [3] O. Hasvold, N. Storkersen, Electrochemical power sources for unmanned underwater vehicles used in deep sea survey operations, *J. Power Sources* 96 (2001) 252–258.
- [4] K. Kordesch et al., Intermittent use of a low-cost fuel cell-hybrid for electric vehicles, *J. Power Sources* 80 (1999) 190–197.
- [5] G. Milazzo, et al., *Tables of Standard Electrode Potentials*, Wiley, New York, NY, 1978.
- [6] E.G. Dow et al., Enhanced electrochemical performance in the development of the aluminum/hydrogen peroxide semi-fuel cell, *J. Power Sources* 65 (1997) 207–212.
- [7] P. Vermeiren et al., Zirfon: a new separator for Ni–H₂ batteries and alkaline fuel cells, *Int. J. Hydrogen Energy* 21 (8) (1996) 679–684.

- [8] R.R. Bessette et al., A study of cathode catalysis for the aluminum/hydrogen peroxide semi-fuel cell, *J. Power Sources* 80 (1999) 248–253.
- [9] K.B. Sarangapani et al., Aluminum as anode in primary alkaline batteries. Influence of additives on the corrosion and anodic behavior of 2S aluminum in alkaline citrate solution, *J. Appl. Electrochem.* 14 (1984) 475–480.
- [10] W. Bohnstedt, The influence of electrolyte additives on the anodic dissolution of aluminum in alkaline solutions, *J. Power Sources* 5 (1980) 245–253.
- [11] R.R. Bessette et al., Development and characterization of a novel carbon fiber based cathode for semi-fuel cell applications, *J. Power Sources* 96 (2001) 240–244.