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A Hybrid Aluminum/Hydrogen/Air Cell—Common Cathode

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Abstract: Metal/Air batteries are considered to be promising electricity storage devices given their compactness, environmental benignity and affordability. As a commonly available metal, aluminum has received great attention since its first use as an anode in a battery. Its high specific energy (even better volumetric energy density than lithium) makes it ideal for many primary battery applications. However, the development of Al/Air cell with alkaline electrolyte has been lagged behind mainly due to the unfavorable parasitic hydrogen generation. Herein, we designed and constructed a novel Al/H_2/Air tandem fuel cell to turn the adverse parasitic reaction into a useful process. The system consists of two anodes, namely, aluminum and hydrogen, and one common air-breathing cathode. The aluminum acts as both the anode for the Al/Air sub-cell and the source to generate hydrogen for the hydrogen/air sub-cell. The aluminum/air sub-cell has an open circuit voltage of 1.45 V and the H_2/Air sub-cell of 0.95 V. We demonstrated that the maximum power output of aluminum as a fuel was largely enhanced by 31% after incorporating the H_2/Air sub-cell with the tandem concept. In addition, a passive design was utilized in our tandem system to eliminate the dependence on auxiliary pumping sub-systems so that the whole system remained neat and eliminated the dependence of energy consuming pumps or heaters which were typically applied in micro fuel cells.

Key words: Al/Air battery, hydrogen fuel cell, passive fuel cell, utilization efficiency, tandem fuel cell.

1. Introduction

Aluminum is a highly promising energy carrier, based on its high theoretical specific energy of 8.1 kWh/kg, a theoretical voltage of 2.73 V in alkaline electrolyte, and a capacity of 2.98 Ah/g. Aluminum has long attracted attention as an anode for energy storage and conversion devices since its first use in the Buff cell in 1857 [1]. However, its application has been limited by the inherent hydrogen generation of the aluminum anode in aqueous electrolytes. Al/Air batteries are thus designed as reserve systems with the electrolyte added just before use or as mechanically rechargeable batteries by replacing aluminum anodes appropriately [2]. The appropriate anodic and cathodic reactions of the Al/Air cell in alkaline electrolyte with standard redox potentials against the standard Ag/AgCl RE (Ag/AgCl reference electrode) are as follows [3]:

$$\text{Anode: } \mathrm{Al(OH)_4}^{-} + 3\mathrm{e}^{-} \leftrightarrow \mathrm{Al} + 4\mathrm{OH}^{-} (\mathrm{E}^{0} = -2.55\ \mathrm{V}) \quad (1)$$

$$\text{Cathode: } \mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e}^{-} \leftrightarrow 4\mathrm{OH}^{-} (\mathrm{E}^{0} = 0.18\ \mathrm{V}) \quad (2)$$

In addition, the parasitic reaction in strong alkaline, also called self-discharge or self-corrosion reaction, at the anode is:

$$\mathrm{Al} + 3\mathrm{H_2O} + \mathrm{OH}^{-} \rightarrow \mathrm{Al(OH)_4}^{-} + \frac{3}{2}\mathrm{H_2} \uparrow \quad (3)$$

This parasitic reaction results in lower anode efficiencies, because it competes with the anodic electrochemical reaction (1) and reduces the energetic output below theoretical values [4]. Intensive efforts

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have been spent to inhibit or even remove the wasteful self-corrosion of the Al/Air sub-cell. Two traditional methods have being applied to make aluminum less corrosive, including doping aluminum with other elements [5-9] and modifying the electrolytes by adding inhibitors, additive agents or complex agents [10-13]. Another way to tackle the self-corrosion issue is to use neutral (saline) electrolyte rather than strong alkaline like NaOH solution [14]. However, such cells suffer from low voltage output (usually considerably lower than theoretical value) due to the sluggish oxidation reaction of aluminum in saltwater. The decrease in the reversible electrode potential is mainly caused by the protective oxide film (Al_2O_3) on aluminum surface [6].

Here in this study, we report a novel approach to tackle the self-discharge issue of Al/Air electrochemical cells. Our elaborately designed cell can utilize the hydrogen generated in aluminum self-discharge reactions to directly fuel an incorporated H_2/Air sub cell on site. Such an approach integrates both an Al/Air sub-cell and a H_2/Air sub-cell into one system where H_2 is supplied by the parasitic reaction of Al/Air sub-cell. By integrating a hydrogen anode into the system, the parasitic reaction can be a beneficial process and hydrogen can be utilized as an energy source rather than a waste. Therefore, the energy utilization efficiency of the aluminum can be highly improved.

2. Experimental

The configuration of the tandem Al/H_2/Air fuel cell is illustrated in Fig. 1. We employed a three-layer device structure, consisting of an Al layer at the

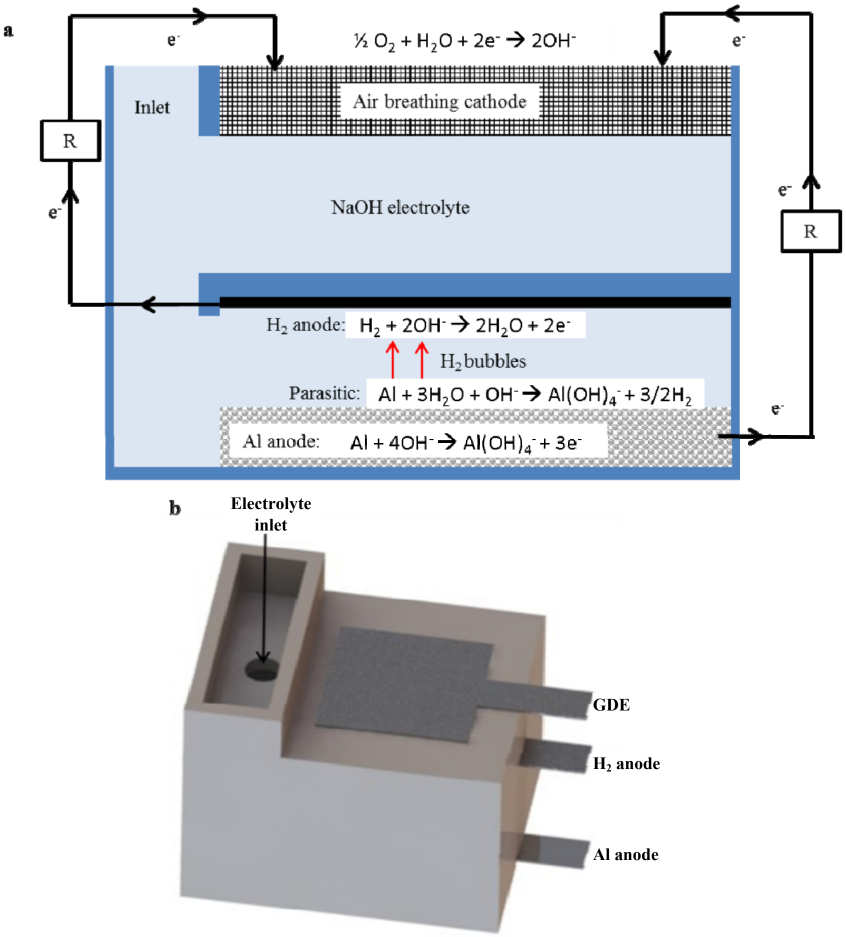

Fig. 1 Structure of the whole tandem cell: (a) schematic of the Al/H_2/Air tandem cell (cross-section view; not drawn to scale); and (b) 3D drawing of the real model.

bottom, a H_2 anode layer in the middle, and a GDE (gas diffusion electrode) as the common cathode on the top. Once H_2 is generated on the Al surface, it will bubble up to the H_2 anode layer and to be oxidized on the Pt-catalyst surface.

The system design was carried out with the 3D drawing software Solid Works®. The frame of the tandem cell was fabricated with a rapid prototyping machine using a corrosive-resistant polymer material. Electrodes were manually integrated into the cell later. A commercialized standard GDE (Hesen, Shanghai) was applied in this cell with Pt loadings of 2 mg Pt/cm^2. The H_2 anode was a carbon paper with the same Pt loadings. An electrochemical station (CHI660D) was set up to characterize the performance of each fuel/oxidant couple. The cell was filled with 60 mL1 M NaOH (sodium hydroxide) solution. Although KOH exhibits higher ionic conductivity than NaOH, NaOH is preferred because the aluminum oxidation product ($NaAl(OH)_4$) can be recycled through the available aluminum industry system via the Bayer process [15]. Sufficient amount of electrolyte was injected into the system to ensure it can operate stably for a relatively long period. An Ag/AgCl reference electrode (Leici, Shanghai) was placed at the inlet and immersed into the electrolyte of the whole system to measure the potential of each electrode. The inlet was connected to different electrodes through the ionic conductive electrolyte as shown in Fig. 1. The effective area for each electrode is approximately 2 cm^2. Once the electrolyte solution was injected into the system, H_2 was generated continuously and bubbled up to the H_2 anode. Both the Al/Air and H_2/Air single cells were characterized using the electrochemical station in situ. The single electrode polarization was measured by techniques presented by Kenis et al. [16]. The voltage-current performance of the Al/Air sub-cell was measured by the linear sweep voltammetry. Unused H_2 then exited the system through the inlet. All experiment was conducted under SATP (standard ambient temperature and pressure).

3. Results and Discussion

Fig. 2a shows the polarization of the Al/Air sub-cell. The Al/Air sub-cell has an open circuit voltage (V_{OC}) of 1.45 V and a short circuit current (I_{SC}) of 40 mA. The peak power ($P_{\max}$) is 14 mW when the current output is 23 mA. The polarization is basically a linear line, which indicates that the cell's performance is dominantly limited by the ohmic loss of the cell. This speculation can be further confirmed by results of the single electrode characterization as shown in Fig. 2b. The potential of Al anode changes linearly from –1.45 V to –0.74 V and that of GDE from 0 to –0.74 V. The theoretical standard electrode potential of reaction (1) vs. Ag/AgCl reference electrode is –2.55 V. However, the measured V_{OC} of Al anode is only –1.45 V, which indicates a large gap of 1.1 V. This is consistent with the conclusion reported in the literature that the Al anode reaction in aqueous alkaline electrolyte experiences severe activation loss because of the blockage of the Al_2O_3 film on Al surface and parasitic corrosion reactions [17, 18]. In contrast, the GDE experiences relatively small activation loss of 0.18 V, which indicates a good quality of the air-breathing cathode.

To the H_2/Air sub-cell, the corresponding anodic and cathodic reactions with standard electrode potentials against Ag/AgCl reference electrode are presented as below:

$$\text{Anode: } 2\mathrm{H_2O} + 2\mathrm{e^-} \leftrightarrow \mathrm{H_2} + 2\mathrm{OH^-}\ (\mathrm{E^0} = -1.05\ \mathrm{V}) \tag{4}$$

$$\text{Cathode: } \frac{1}{2}\mathrm{O_2} + \mathrm{H_2O} + 2\mathrm{e^-} \leftrightarrow 2\mathrm{OH^-}\ (\mathrm{E^0} = 0.18\ \mathrm{V}) \tag{5}$$

The polarization curve of the H_2/Ar sub-cell is shown in Fig. 3a. The cell also exhibits a linear polarization with V_{OC} of 0.95 V and I_{SC} of 20 mA. The measurement of H_2 anode polarization experienced some disturbance since H_2 bubbles were continuously generated from the Al plate while unreacted H_2 escaping from the system. The power peaks at 4.3

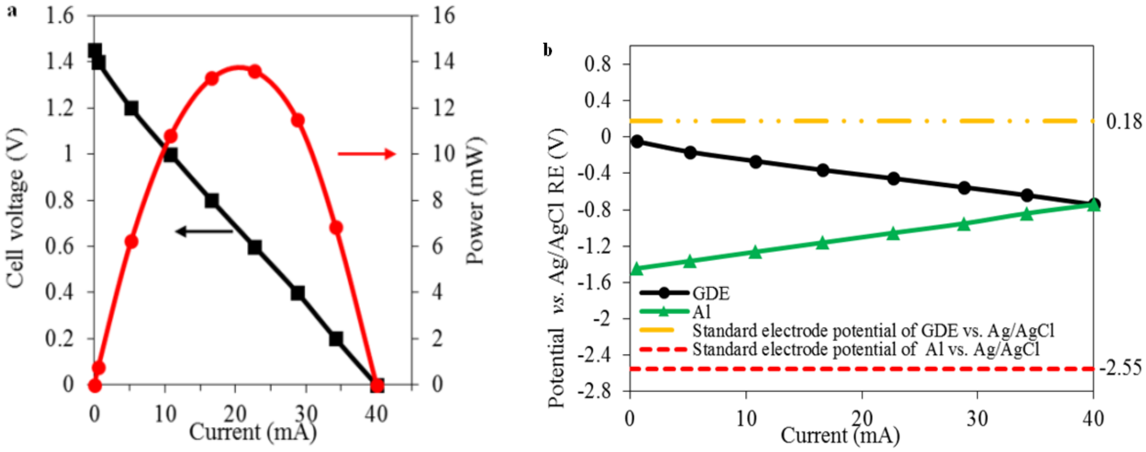

Fig. 2 Test results of the Al/Air sub-cell: (a) I-V polarization (black) and power output (red) curves of the Al/Air sub-cell; and (b) single electrode polarization data of the Al/Air sub-cell measured vs. the Ag/AgCl reference electrode.

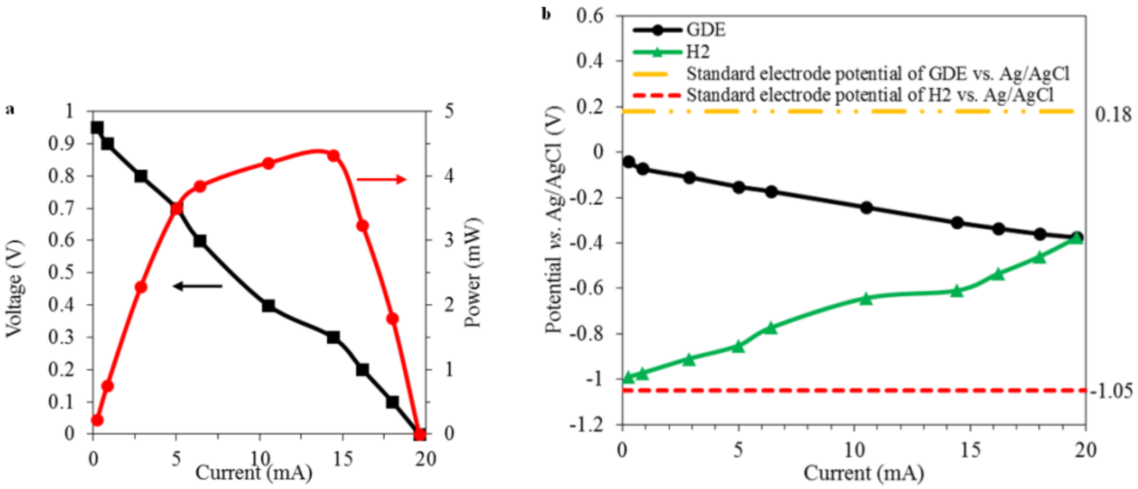

Fig. 3 Test results of the H_2/Air sub-cell. (a) I-V polarization (black) and power output (red) curves of the H_2/Air sub-cell; and (b) singel electrode polarization data of the H_2/Air sub-cell measured vs. the Ag/AgCl reference electrode.

mW when 14 mA current is drained out. Fig. 3b shows the single electrode characterization results of H_2 anode and GDE, respectively. Both electrodes experience small activation loss at anode of 0.05 V and at GDE of 0.18 V, respectively. The potential of anode changes from –0.99 V to –0.38 V while that of GDE from –0.04 V to –0.38 V.

Taking the peak power output of the H_2/Air sub-cell into consideration, the whole system's maximum power output increased from 14 mW to 18.3 mW, by 30.7%. From the Al utilization rate point of view, the H_2 gas generated by the Al self-corrosion can in principle be fully consumed at the H_2 anode if the electrode reaction area is properly designed. If 4 M NaOH solution is used as electrolyte in the tandem cell, the corrosion rate ($J_{\mathrm{corrosion}}$) of the Al to generate H_2 is around 50-100 mA/cm^2 [19]. $J_{corrosion}$ varies little for a specific concentration of NaOH under different operating voltages. If we take Al electrochemical current rate (J_{Al}) of 100 mA/cm^2 and the H_2 oxidization rate of 50 mA/cm^2 [20], then the optimal area for H_2 anode should double that of Al used in the tandem cell. Actually, this is a conservative calculation. So, an even smaller area of H_2 anode can be integrated into the tandem cell in real design.

The performance of both Al/Air and H_2/Air sub-cells is predominately limited by the system ohmic loss. A rough calculation from the polarization curves indicated the cell resistance was in the range of 20 Ω to 30 Ω. Several factors may contribute to the ohmic loss. For the Al/Air sub-cell, this includes the large spacing (30 cm) beteween the anode and cathode, the H_2 bubble layer on aluminum surface and probably aluminum oxide and aluminum hydroxide thin film layers. In fact, the H_2 bubble layer, and Al_2O_3 and hydroxide layers may block the contact between the electrolyte and electrodes. Aluminum hydroxide, $Al(OH)_3$, which is thought to be an intermediate product, is not stable in strong alkaline. The $Al(OH)_3$ film formed electrochemically is soon dissolved chemically by OH^- attack at the film/solution interface to form soluble $Al(OH)_4^-$ [21]. Details of the aluminum anodic dissolution mechanism can be sought in Ref. [21]. H_2 bubbles generated on Al surface may also increase the resistance between the Al anode and electrolyte. Emregul et al. [22] found that the surface structure of aluminum in NaOH solution is porous-like and the accumulation of hydrogen molecules on the aluminum surface causes an increase in resistance. As for the H_2/Air sub-cell, the ohmic loss may also come from the poor contact between the electrolyte and anode. During the experiment, the H_2 gas was observed to partially accumulate on the H_2 anode surface since it cannot be fully depleted, which also results in a poor electrode-electrolyte.

Compared with the hydrogen production using aluminum and aluminum alloys [17], our electrochemical tandem cell is multi-functional: (1) using alumunium to generate electricity; (2) utilizing the self-corrision reaction of the Al anode in alkaline to produce H_2; and (3) integrating a H_2/O_2 fuel cell in the same device to consume the H_2 on site. Another notable advantage of our tandem system is that it operates passively without any auxcillary instruments like pumps to inject fuel and oxidant, which are typically required in fuel cells. In addition, the system can be turned on or off by inserting the aluminum plate into or taking out of the system. In the same way, the cell can be mechananically recharged by replacing the aluminum and electrolyte.

4. Conclusions

In summary, we set up a novel tandem cell to tackle the self-corrosion problem of Al/Air batteries from a fresh angle. In our system, the self-corrosion issue of Al in strong alkaline electrolyte was turned into a beneficial process to fuel an additional H_2/Air sub-cell. We demonstrated that the maximum power output of aluminum as a fuel was greatly enhanced by 31% after incorporating the H_2/Air sub-cell with the tandem concept. In addition, a passive design was utilized in the tandem system to eliminate the dependence on auxillary sub-systems so that the whole system remained neat and eliminated the dependence of energy consuming pumps or heaters which were typically applied in micro fuel cells. In our future work, we will try to further improve the performance of the system, by applying, for example, smaller spacing, better contacts and/or higher concentration of electrolyte.

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