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A hybrid aluminum/hydrogen/air cell system

Lei Wang [a], Wentao Wang [a], Guandong Yang [a], Dong Liu [a], Jin Xuan [b,c], Huizhi Wang [a], Michael K.H. Leung [b], Fude Liu [a,d,*]

[a] Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, China
[b] Ability R&D Energy Research Centre, School of Energy and Environment, City University of Hong Kong, Hong Kong, China
[c] School of Mechanical and Power Engineering, East China University of Science and Technology, China
[d] Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy of Sciences, Suzhou 215123, China

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ABSTRACT

A hybrid aluminum/hydrogen/air cell system is developed to solve the parasitic hydrogen-generating problem in an alkaline aluminum/air battery. A H_2/air fuel cell is integrated into an Al/air battery so that the hydrogen generated by the parasitic reaction is utilized rather than wasted. A systematic study is conducted to investigate how the parasitic reaction and the added H_2/air cell affect the performance of the aluminum/air battery. The aluminum/air sub-cell has an open circuit voltage of 1.45 V and the hydrogen/air sub-cell of 1.05 V. The maximum power density of the entire hybrid system increases significantly by ~20% after incorporating a H_2/air sub-cell. The system maximum power density ranges from 23 to 45 mW cm^{-2} in 1–5 M NaOH electrolyte. The hybrid system is adaptable in concentrated alkaline electrolyte with significantly improved power output at no sacrifice of its overall efficiency.

1. Introduction

Metal–air batteries promise to be the next-generation energy storage technologies and have been at the forefront of energy research for years. Aluminum, with a high energy density of 8.1 kWh kg^{-1} and a theoretical potential of 2.35 V in alkali electrolyte *vs.* standard hydrogen electrode (SHE), has emerged as one of the most promising anode candidates. As the most abundant metal element on Earth, aluminum represents the second largest metal market in the world, and has a much lower price than most base metals. Compared with gaseous fuels like hydrogen, aluminum is easier to transport and store, and can be recycled through industrial retreatment. Because of all these advantages, aluminum is considered as a highly promising energy carrier [1,2]. Among various types of aluminum batteries, the aluminum/air battery has the highest theoretical energy density and a relatively low material cost [3]. However, although the potential of aluminum was keenly anticipated in the 1970s, enthusiasm diminished due to the destructive self-corrosion (parasitic reaction) problem [1,4]. With the advancement in catalyst engineering and understanding air-breathing cathodes, researchers have recently

* *Corresponding author*. Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, China. Tel.: +852 2859 2631; fax: +852 2858 5415.
E-mail address: fordliu@hku.hk (F. Liu).

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Nomenclature

V_{H_2}	volume of H_2, mL
ε	aluminum utilization efficiency, %
r_{H_2}	H_2 evolution rate per area of aluminum, $\mu L\ s^{-1}\ cm^{-2}$
I_{main}	desirable main current, A
I_{ox}	aluminum oxidation current, A
I_{pa}	parasitic reaction current, A
$E_{corrosion}$	aluminum corrosion potential, V
V_{OC}	open circuit voltage, V
V_{Al}	aluminum working voltage *vs.* Ag/AgCl, V
$V_{Al\ cell}$	aluminum/air sub-cell voltage, V
$V_{H_2\ cell}$	hydrogen/air sub-cell voltage, V
$V_{Al\ OC}$	aluminum anodic potential at the open circuit condition, V
$V_{GDE\ OC}$	oxygen reduction potential at the open circuit condition, V
i_{sc}	short circuit current density, mA cm^{-2}
P_{max}	maximum power density, mW cm^{-2}
ε_{real}	real efficiency of a fuel cell, %
$\varepsilon_{thermal}$	reversible thermodynamic efficiency, %
$\varepsilon_{voltage}$	voltage efficiency of the fuel cell, %
ε_{fuel}	fuel utilization efficiency, %
ε_{system}	hybrid system's real efficiency, %
$\varepsilon_{Al\ cell}$	aluminum/air cell's real efficiency, %
$\Delta\hat{g}$	Gibbs free energy change for the reaction, J mol^{-1}
E^0	standard-sate reversible voltage, V
$\Delta\hat{h}$	heating value of the fuel, J mol^{-1}
V	cell working voltage, V
A	effective electrode area, cm^2

begun to evaluate aluminum/air batteries again for electric vehicles [5]. In 2013, an Israeli company demonstrated an aluminum/air battery pack that powered an electric vehicle for 1000 miles [6].

The inherent dissolution of aluminum in basic solution is detrimental to an aluminum/air battery. The self-corrosion can cause not only a lower utilization efficiency of aluminum, but also possible battery explosion as a result of hydrogen buildup. Researchers have tried to lower the self-corrosion rate through alloying aluminum with selected elements [7–11], adding inhibitors into the electrolyte [12–17], or using expensive high-purity aluminum (purity ≥99.995%) [5,18]. However, these methods have shown limited success and increased the cost and complexity of the battery. Herein, we take a novel approach to handle the parasitic hydrogen generation problem in alkaline aluminum/air batteries and demonstrate a promising hybrid system using kitchen-type aluminum for electricity generation. A hydrogen/air fuel cell is integrated into an aluminum/air battery in a compact membraneless design so that the hydrogen generated by aluminum self-corrosion can be utilized as fuel for the hydrogen/air sub-cell. There are several advantages of the hybrid Al/H_2/air cell system: 1) it turns the parasitic hydrogen evolution reaction into a beneficial process; 2) it increases the power output of the entire system; 3) it minimizes the possibility of H_2 explosion through consuming it on-site in a H_2/air sub-cell; 4) it has relatively low system cost because no expensive high-purity aluminum and fuel cell membrane are used; and finally, 5) it is adaptable in concentrated alkali electrolyte without overall efficiency degradation.

2. Experimental

The experiment was divided into two parts. The first part examined the aluminum corrosion. Because of the parasitic reaction, the aluminum utilization efficiency has consistently been much lower than expected. Thus, it is essential to understand how aluminum utilization efficiency relates to the working potential of aluminum and to the concentration of electrolyte. The second part tested the hybrid system performance. To explore cost-effective fuel source, ordinary kitchen aluminum foil (~16.2 μm thick) was employed in two experiments rather than specially formulated aluminum alloys. The foil composition was studied using scanning electron microscopy with energy-dispersive X-ray (SEM/EDX) analyses to have a uniform Al purity of 97.6 wt% (impurities: O 1.13, Fe 0.68, and Ag 0.59 wt%). All experiments were conducted under standard ambient temperature and pressure (SATP). Each experiment was repeated at least three times to ensure the reliability and accuracy of results.

2.1. *Aluminum corrosion investigation*

An apparatus was set up, similarly to the methods in Refs. [7,19], to measure the volume and evolution rate of hydrogen (Fig. 1). Al foil was cut into small pieces of 2 × 2 cm^2 with weight of 17.508 mg. A plastic dish with a measuring cylinder was filled with abundant alkaline electrolyte. NaOH electrolyte is preferred because it favors the industrial Hall–Héroult process to re-produce Al [1,18], although KOH exhibits a better conductivity. The electrolyte was continuously washed with H_2 gas before use to make sure it reached dissolved hydrogen saturation. An upside-down Y-shaped cylinder was used to collect and measure the amount of H_2 generated on the aluminum surface. A syringe was applied to suck the electrolyte into the cylinder to reach a height as the starting reading point, and then the tube was shut with a clip. Finally,

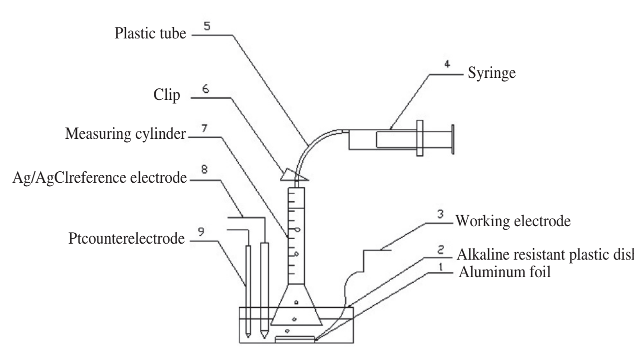

Fig. 1 – Schematic of the apparatus used to measure the volume and generation rate of hydrogen.