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A high performance dual electrolyte aluminium-air cell

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Abstract

Energy storage capacity has been a major limiting factor in pursuit of increasing functionality and mobility for portable devices. To increase capacity limits, novel battery designs with multi-electron redox couples and increased voltages have been listed as a priority research direction by US Department of Energy. This study leverages the benefits of microfluidics technology to develop a novel type of mixed-pH media aluminium-air cell, which incorporates the advantages of aluminium's trivalence and mixed-pH thermodynamics. Experimentally, an open circuit potential of 2.2 V and a maximum power density of 176 mW/cm² are measured from the new cell, which are respectively 37.5% and 104.6% higher compared to a conventional alkaline aluminium-air cell.

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Keywords: Aluminium anode, Dual electrolyte; Co-laminar flows

1. Introduction

Energy storage has become a growing global concern over the past decade as a result of drastic consumption of non-renewable fuels, along with increasing energy demands from daily lives and industrial manufacturing.[1,2] This calls for more efficient energy storages and power sources with higher energy densities and lower costs.

Aluminium (Al)-air cells, working with an inexhaustible cathode reactant (oxygen from air), hold certain promise as an alternative to existing commercial batteries because of their unsurpassable capacity and energy densities.[3] Compared with other active materials for metal-air cells, such as lithium, magnesium and zinc, Al has the highest volumetric capacity density of 8.04 Ah cm⁻³ contributed by the trivalence of aluminium ions. Additional benefits of Al are the environmental friendliness, low price and the existence of a large base of raw materials.[4] In past decades, great emphasis had been focused on Al-

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air cells working with a single alkaline or brine electrolyte.[5-7] In conventional single-alkaline-electrolyte Al-air cells, Al exhibits a theoretical energy density of 8.10 Wh g^{-1} . [3,8]

Different from single-electrolyte cell, a concept of mixed-pH dual-electrolyte design for increasing the thermodynamic potential has been studied in H_2/O_2 fuel cells.[9] A mixed-pH media employs alkaline and acid environment for anode and cathode, respectively. Based on laminar flow,[10,11] the interface between two different fluids could be well maintained in a microchannel, without the use of polyelectrolyte membrane(PEM). This membraneless system could also eliminate the intrinsic problems of PEM, such as desiccation, tearing and deterioration, and also reduce the cell cost.

In this work, the performance of a novel dual-electrolyte Al-air cell, built on a Y-shape membraneless platform, is demonstrated. In this dual-electrolyte system, streams of alkaline anolyte and acid catholyte flow separately with minimal convective mixing. A detailed comparison of the performance between dual- and single-electrolyte is presented in following sections. In addition, a durability test of this dual-electrolyte Al-air cell was carried out to show its long term stability in the terms of current and voltage.

2. Experimental setup

2.1 Cell design and fabrication

Figure 1 shows a schematic illustration of the Y-shape membraneless Al-air cell structure. The cell structure consists of three PVC layers cut by carbon dioxide laser ablation system (VLS 2.30, Universal Laser System). The bottom and top layer each has a rectangle window around the edge of channel cut out for electrodes to contact with electrolyte. The active projected electrode area is 0.0364 cm^2 ($0.07 \text{ cm} \times 0.52 \text{ cm}$). The top layer seals the assembly with two inlets and an outlet for fluidic access. Two streams of electrolyte are delivered to the 1.5 mm width channel in the middle layer by a syringe pump (LSP02-1B, LongerPump) at a flow rate of 1300 ul/min using 1.5 mm tubing (Dragon Heart Medical Devices Co., LTD.) bonded to the ports with quick dry epoxy. The three PVC layers have a thickness of 0.1 mm , 1 mm and 0.1 mm , respectively, and are adhered using double-side adhesive tape.

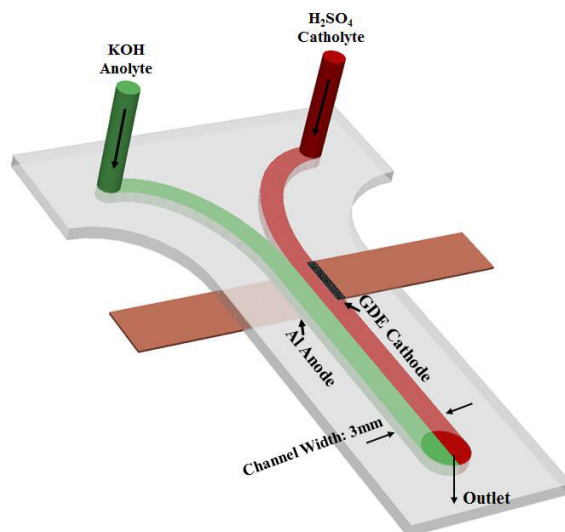


Figure 1 Schematic illustration of Y-shape membraneless Al-air cell structure

2.2 Electrode and Electrolyte

Electrolytes of aqueous KOH and H₂SO₄ solutions with different concentrations (1M, 2M and 3M) were prepared by dissolving KOH pillars ($\geq 85\%$, Sigma Aldrich) and H₂SO₄ (95-97%, Sigma Aldrich) in 18.2 M Ω deionized water (Thermo Scientific). Al bulk with a purity of 99.9% was used as anode. The cathode was a gas diffusion electrode (GDE), bought from Shanghai Hesen Company. Carbon paper (HCP120, Hesen) with a microporous carbon layer serves as the catalyst support and gas diffusion layer. The catalyst powder, Pt/C (60 wt.% Pt, Johnson Matthey), is dispersed by dispersion solution (ethanol and water, 1:1 volume ratio) and 5wt% Nafion solution first, then sonicated for 1h, and finally sprayed on the carbon paper with an overall loading of 2mg/cm² Pt/C for cathode. Copper foil was used to connect the electrodes with external circuit.

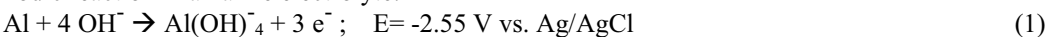
2.3 Cell testing

Electrochemical measurements were carried out under room temperature and ambient atmospheric pressure. The polarization curves were obtained by potentiostatic current measurement at every 0.2 V for 150 s from short circuit to open circuit potential by a CHI 660E electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd.). The average value of the current data in the last 50 seconds was used to represent the cell current at a certain voltage. An Ag/AgCl(KCl) electrode (Shanghai Lei-ci Co., Ltd.) was used as a reference electrode to acquire a single-electrode potential of the cell. The data was recorded *in situ* by a digital multimeter (15B, Fluke Corporation). Electrochemical impedance spectroscopy (EIS) of dual-electrolyte Al-air cell with electrolytes was taken in the frequency range of 120 kHz-100 mHz, with a signal A.C. amplitude of 5 mV at 1.4 V for dual-electrolyte Al-air cell, which is around the peak power density voltage.

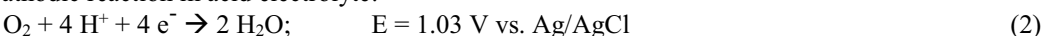
3. Result and discussion

The half-cell reactions of the Al-air cell in different electrolytes are shown as follows:[12,13]

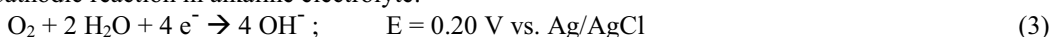
Anodic reaction in alkaline electrolyte:



Cathodic reaction in acid electrolyte:



Cathodic reaction in alkaline electrolyte:



The Al-air cell with dual electrolyte has a theoretical voltage of 3.58 V, which is 830 mV higher than that of single-alkaline-electrolyte cell. The theoretical energy density considering only Al also increases from 8.10 Wh g⁻¹ in conventional single electrolyte to 10.54 Wh g⁻¹.

3.1 Single-Alkaline-Electrolyte Al-Air Cell

Figure 2(a) presents the polarization (j-V) and power density curves of Al-air cells working with single alkaline electrolyte (1M, 2M and 3M KOH solutions). Single-alkaline-electrolyte Al-air cells exhibit linear polarization curves with OCPs around 1.6 V. As one can see, increasing the concentration of electrolyte leads to a significant increase in short-circuit current density (J_{sc}). Cell with 3M KOH electrolyte obtains a J_{sc} of 176 mA/cm², corresponding to a low internal resistance of 9.38 ohm/cm². This is due to higher reaction rate on electrode and conductivity in electrolytes with higher concentration. The

cells obtain the peak power output around 0.8V. The effects of electrolyte concentration are also reflected by a peak power density increment from 46 to 86 mW/cm^2 when concentration increases from 1M to 3M.

Figure 2(b) shows the single-electrode potential curves. In open circuit, the anodic and cathodic potential is around -1.5 V and 0.1 V vs Ag/AgCl, respectively. Concentration has a slight influence on the potential of each electrode. Potential loss of around 1 V takes place on the Al side. This due to the formation of a protective oxide film and generation of hydrogen from corrosion of Al in alkaline environment.[8] Both of these factors contribute significantly to the potential loss on the Al side. Over the whole current range, the anode potentials change prominently, indicating a great ohmic loss of anode.

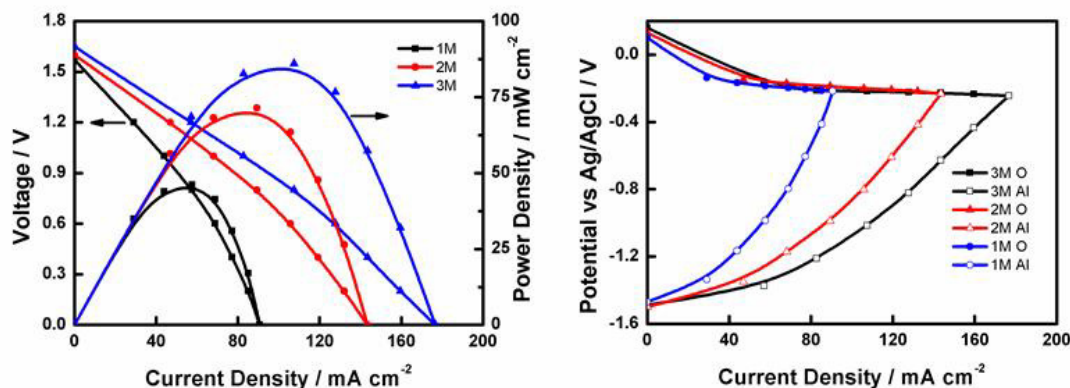


Figure 2 (a) Polarization (j-V) curves and power density curves (b) Single-electrode potential curves of Al-air cell with single alkaline electrolyte.

3.2 Dual Electrolyte Al-air Cell

Figure 3 (a) shows polarization (j-V) and power density curves of the dual-electrolyte Al-air cells working with different concentrations of KOH as anolyte and H_2SO_4 as catholyte. OCPs around 2.2 V are achieved, which is 600 mV higher than that in single-electrolyte cells. J_{sc} are also improved with the dual-electrolyte system. Working with 3M electrolyte, the cell has a J_{sc} of 207 mA/cm^2 , which is 17.6% higher than that in the single-alkaline-electrolyte system. Voltage of the peak power density is around 1.4V. The peak power density obtained in dual-electrolyte is 176 mW/cm^2 , which is twice of that in the single-electrolyte cell under analogous conditions.

Single-electrode potential curves (Figure 3(b)) present more positive potentials of cathode in acid catholyte. Though the anode has the similar property as that in single-electrolyte system, this helps cells to achieve higher OCPs. The overpotential on cathode is about 0.3 V, compared to theoretical value, which is much lower than the Al side. Over the whole current range, cathode side exhibits a quite low resistance. With an improvement of potential on cathode, the restriction of Al become more significant and retards the increase of current density under lower voltage, leading to a non-linear shape of polarization curves.

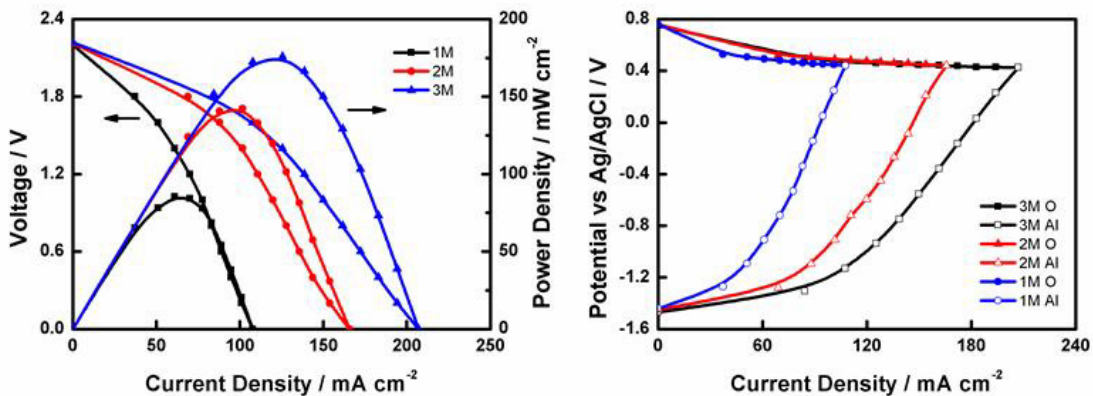


Figure 3 (a) Polarization (j-V) curves and power density curves (b) Single-electrode potential curves of Al-air cell with dual electrolyte.

The EIS plots of Al-air cell with different electrolytes concentrations are shown in Figure 4 (a). The shapes of impedance plots are characterized by a high frequency capacitive loop and a low-frequency capacitive loop.[14] Inspection of the figure reveals that an increase in the concentration results in a decrease in the size of the semicircle and impedance. This can be inferred as due to the higher conductivity of higher concentration electrolyte, which is consistent with polarization curves.

Figure 4 (b) shows the open circuit potential stability and the durability of current at the voltage of 1.4, which has the peak power density output. As can be seen, the cell open circuit potential is very stable, with less than 1% fluctuation within the 5000s’ testing. It is interesting to note that the discharge current decreases gradually from 4.50 mA to 3.95 mA for the first 1200s and then gradually increase to a maximum of 5.24 mA. This phenomenon may be caused by the increase of reaction area of Al with electrolyte after the reaction starts.

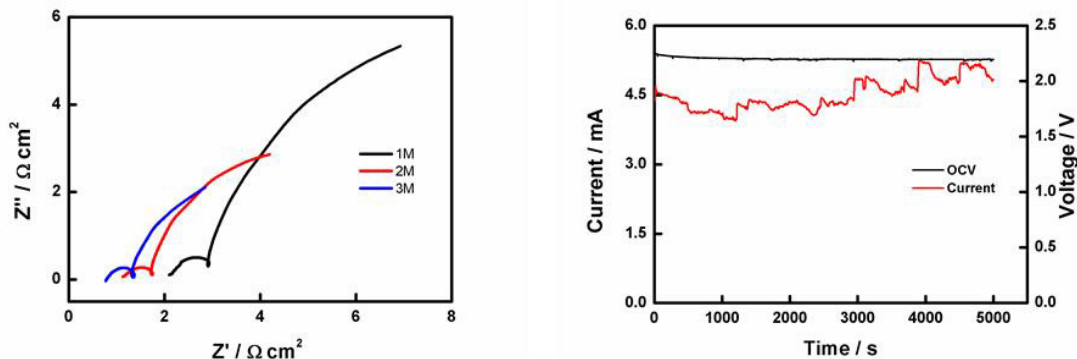


Figure 4 (a) EIS of cell with dual electrolytes and (b) Long term discharge at 1.4V (Voltage of the Peak Power Density)

4. Conclusions

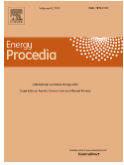
In summary, a novel dual-electrolyte membraneless Al-air cell, built on a Y-shape membraneless platform is presented here to achieve higher cell voltage and power output. The cell employs laminar flow to avoid the use of a membrane. The result shows that, compared with a single-alkaline-electrolyte cell, a dual-electrolyte cell has an advantage of higher open-circuit potentials (600 mV higher) and has superior performance with a peak power density of 175 mW/cm², which is twice that of the values obtained from single alkaline electrolyte Al-air cell. The durability of the dual-electrolyte cell was also demonstrated. A restriction from the Al side is observed in cells, limiting further improvement of current at low voltages. Further works will focus on improving activation of Al in electrolyte.

Acknowledgement

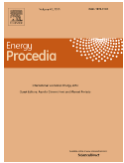
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**Biography**

Prof. Leung received his Ph.D. from the Department of Mechanical Engineering, the University of Hong Kong (HKU). He worked at the Hongkong Electric Co. Ltd. as an environmental engineer for five years before joining HKU in 1993. Prof. Leung is now a full professor of the department specializing in air pollution, renewable energy and energy conservation. He is a specialty chief editor of the Frontiers in Environmental Sciences and editorial board member of several journals including Applied Energy.

**Biography**

Dr. Huizhi Wang received her Ph.D. in Mechanical Engineering from the University of Hong Kong in 2011. She joined the school of Engineering and Physical Science at Heriot-Watt University as an assistant professor since September 2014. Her main research interest focuses on electrochemistry for energy storage and carbon conversion.