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Microfluidic aluminum-air cell with methanol-based anolyte

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Abstract

Aluminum-air cell, with trivalence redox couples, attracts a lot of interest to break the capacity limitation of conventional batteries in pursuit of higher mobility for portable devices. In order to overcome the self-discharge issue of aluminum, a microfluidic aluminum-air cell working with methanol-based anolyte was developed in this work. The operation feasibility of this membraneless cell was first proved. Then, the influences of electrolyte concentration and water content in the methanol-based anolyte on cell performances were investigated. Experimentally, a high discharge capacity density of 2507 mAh/g was achieved at a low current of 0.015 mA.

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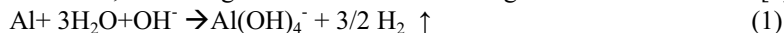
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Keywords: Aluminum-air cell, methanol-based anolyte, microfluidic

1. Introduction

Energy demands of our society increase drastically because of the ever growing economics and technology development. With intense consumption of fossil fuels, a transition from non-renewable fuel-based to a sustainable energy-based society is inevitable. Fuel cells have long been recognized as a promising energy carrier candidate for their high energy and capacity densities, and found usages in various applications in recent decades. [1]

Metal-air cells, generating electricity from the reactions between oxygen and metal materials, achieve remarkable energy densities.[2] Meanwhile, there is no more concern about storage of oxygen in the cells since it could be accessed from the ambient atmosphere. Among different metals, aluminum (Al) has a very high capacity density of 2980 mAh/g, along with its large reserves, attracting considerable interest as anode material for metal-air cells. However, Al undergoes a serious self-discharge in alkaline solutions:[3]



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making the capacity density low in practice. This wasteful self-corrosion leads to an unacceptable high-energy loss and safety problem during standby and operation of cells.

In this work, a non-direct counter-flow microfluidic Al-air cell with methanol-based anolyte was developed. During operation, the cell worked with methanol-based anolyte and water-based catholyte to overcome the self-corrosion problem of Al. The diffusion of methanol and water in the channel was firstly investigated to make sure that the crossover of electrolytes has been well controlled. Within the microchannel, the interface between the two electrolytes could be well maintained at an electrolyte flow rate of 1000 $\mu\text{l}/\text{min}$, serving as a virtual membrane to separate the two electrolytes and conduct ions.[4] Then, the influences of the electrolyte concentration and water content in the methanol-based anolyte were investigated.

2. Experimental setup

2.1 Cell design and fabrication

Figure 1 shows the schematic illustration of the non-direct counter-flow microfluidic Al-air cell. The cell structure consists of three Polyvinyl chloride (PVC) layers cut out by a carbon dioxide laser ablation system (VLS 2.30, Universal Laser System, USA). The top layer seals the assembly with two inlets and an outlet for fluidic electrolyte access. The two inlets connect with the anolyte sub-channel and catholyte sub-channel, respectively. On the bottom layer, two square windows are cut out to allow the electrodes to contact with electrolyte. The active projected electrode area is 0.015 cm^2 , and all current and power densities are normalized by this area. The distance between the anode and the cathode is 2.0 mm. Three layers have thickness of 0.1 mm, 0.5 mm and 0.1 mm, respectively, and are adhered with each other by double-side adhesive tape. The electrolyte is pumped into the cell by a syringe pump (LSP02-1B, LongerPump, China), via 1.5 mm tubing bonded to the ports with quick dry epoxy.

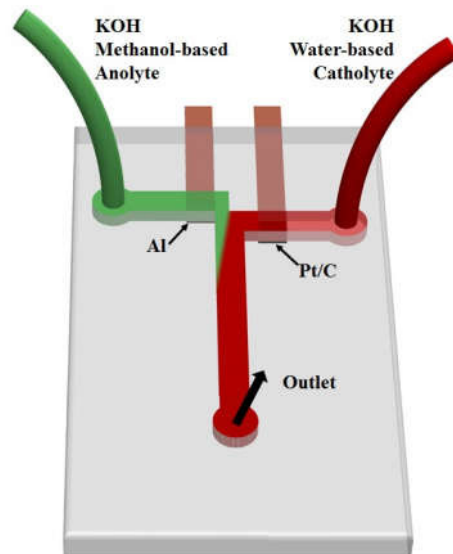


Figure 1 Schematic of the microfluidic Al-air cell with methanol-based anolyte built on non-direct counter-flow configuration.

2.2 Chemicals

Alkaline electrolytes with different concentrations of KOH were prepared by dissolving KOH pellets ($\geq 85\%$, Sigma Aldrich, Hong Kong) in methanol ($\geq 99.9\%$, Merck KGaA, Germany) or 17.9 M Ω deionized water (Barnstead, NANOpure DiamondTM, USA). Low cost kitchen Al foil was used as a cost-effective anode. The compositions of this foil were analyzed by energy-dispersive X-ray on a Hitachi S-4800 microscope to be 99.0% purity of Al with trace amounts of Fe and Ag as impurities. A gas diffusion electrode (GDE) with catalyst loading of 2 mg/cm² Pt/C (Hesen Company, China) was adopted as cathode. Copper foil was used as current collector to connect the electrodes with external circuit.

2.3 Characterization of electrolyte flow

Solutions of bromophenol blue (C₁₉H₁₀O₅Br₄), a methanol/water-ratio-sensitive dye, with a concentration of 1.75 mg/ml were prepared in solvents containing different volume ratios of methanol and deionized water. The solutions were observed by Precentered Fiber Illuminator (Intensilight C-HGFI Nikon, Japan) using yellow fluorescent light with wavelength range of 600-630 nm. At this wavelength range, the methanol solution of C₁₉H₁₀O₅Br₄ was a transparent orange solution while water solution was opaque. The color was gradually transformed when the volume ratios of methanol/water changed. For calibration, colors of C₁₉H₁₀O₅Br₄ solutions with different methanol/water ratios were captured by Illuminator. Then pure C₁₉H₁₀O₅Br₄ methanol solution and water solution were pumped into the cell channel structure to investigate the flow pattern of methanol and water electrolytes at different flow rates.

2.4 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 200s, from open-circuit voltage (OCV) to 0 V, by a CHI 660E electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., China). The average value of the current data in the last 50 seconds of the sampling was used to represent the cell current at a certain voltage. An external AgAgCl (in saturated KCl) electrode (Shanghai Lei-ci Co., Ltd., China) was used as reference electrode to acquire single-electrode potentials of the cell. The potential data was recorded *in situ* by a digital multi-meter (15B, Fluke Corporation, USA).

To evaluate the capacity of Al-air cell, galvanostatic discharging was performed at a small current of 0.015 mA, corresponding to a current density of 1.0 mA/cm². The specific capacity of Al was calculated as:

$$C=(I \cdot t)/M, \quad (2)$$

where I is the discharging current used (i.e. 0.015 mA); t is discharging time and M is mass of Al consumed.

3. Result and discussion

3.1 Characterization of electrolyte flow pattern

Due to a high mutual solubility of methanol and water, the operating condition to avoid crossover of methanol and water electrolyte in the present microfluidic cell structure needs to be critically determined. Figure 2 shows the visualization optical micrographs of methanol and water-based electrolyte flow pattern in this cell structure as a function of flow rates, from 100 μ l/min to 1000 μ l/min. A diffusion

mixing segment could be easily observed in the middle part. By increasing flow rate, the influence of convective flux became greater than the opposite diffusive mixing flux, shrinking the mixing segment of electrolyte in this counter-flow architecture. With the increase of flow rate to 1000 $\mu\text{l}/\text{min}$, the boundary of the diffusion segment would be within the range between the two electrodes, indicating that the crossover of electrolytes to opposite electrode was inhibited.

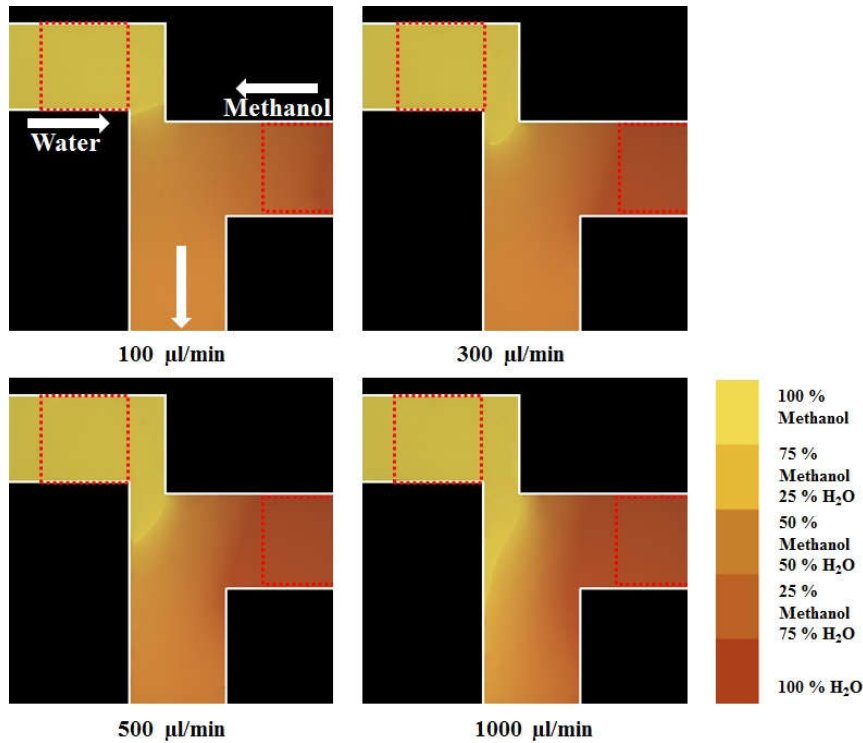


Figure 2 Optical images of diffusion area of methanol and water in the microchannel as a function of flow rate. Red squares are electrode positions.

3.2 Cell performance

3.2.1 Polarization and power characteristics

Figure 3 shows the cell performance including polarization and power density curves as a function of the electrolyte KOH concentrations and the percentages of water in methanol-based anolyte. As can be seen, the cell with 1 M electrolyte had an OCV of 1.36 V, with anodic and cathodic potential of -1.31 V and 0.05 V vs. AgAgCl, respectively. With the concentration increased to 4 M, the OCV raised to 1.59 V. This increase was mainly due to the activation of the anode side, which was -1.57 V vs. AgAgCl with 4 M electrolyte. However, a mass transportation limit appeared at lower voltage. Cell with 3 M electrolyte showed the highest short-circuit current density of 8.63 mA/cm^2 .

As shown in Figure 3 (c) and (d), the percentage of water had a slight influence on the OCV (1.45 ± 0.05 V). The polarization curves presented in Figure 3 (c) showed an increase in cell output with higher water percentages. The short-circuit current densities sharply increased from 1.25 mA/cm^2 for 0% to 55.2 mA/cm^2 for 60%. The electrical performance of fuel cell was significantly enhanced by the addition of

water in the KOH methanol-based anolyte. This improvement was attributed to (i) the decreased viscosity of the electrolyte solution promoting mass transfer, (ii) activation of the dissolution process of passive film on Al surface after discharging and (iii) the improvement of conductivity of electrolyte solution. As can be seen from the single-electrode polarization curve, the Al anode rather than the GDE is the limiting factor on the cell performance.

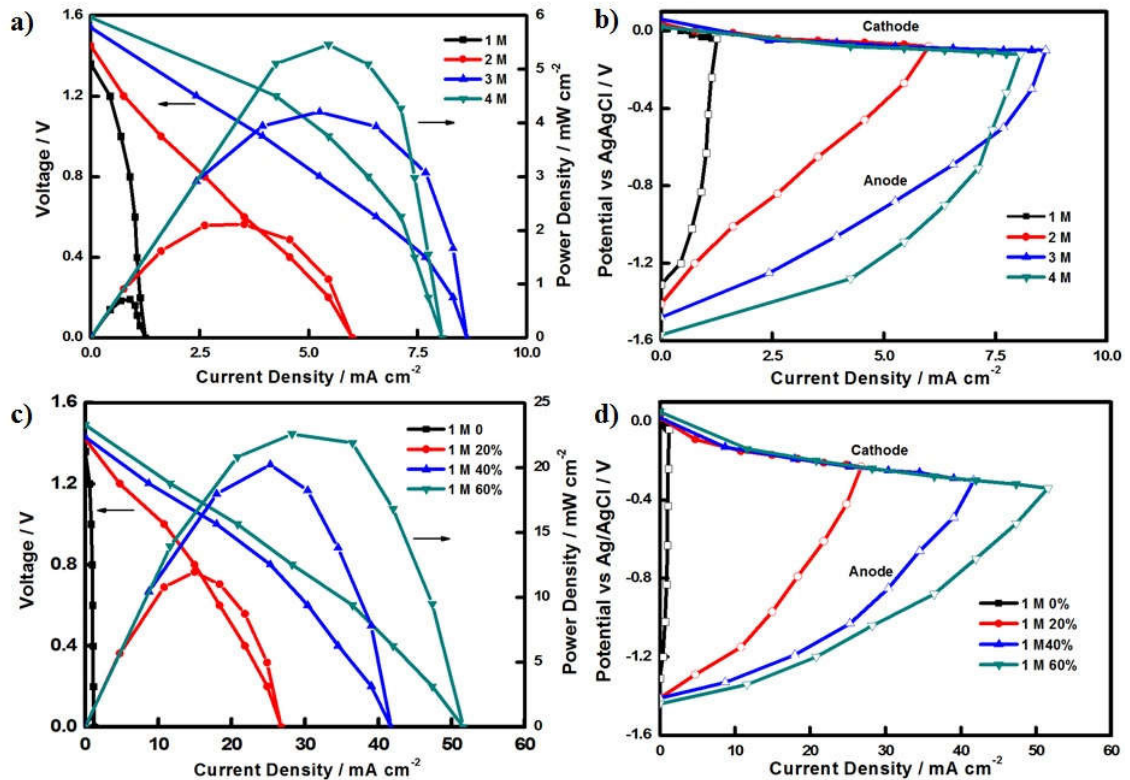


Figure 3 Performance of Al-air cells with different concentrations of KOH methanol solutions as anolyte: (a) Polarization curves and power density vs. current density curves, (b) Single-electrolyte polarization curves; with different water content in the KOH methanol solutions anolyte: (c) Polarization curves and power density vs. current density curves; (d) Single-electrolyte polarization curves.

3.2.2 Discharge characteristics

The discharge curves of the Al-air cell with methanol-based anolyte reveal that Al can exhibit much higher coulombic efficiency in methanol-based electrolytes than in water-based ones, which is consistent with the findings in Wang et al.[5] In fact, the hydrogen generation was barely observed in the cell with methanol-based anolyte, indicating that the parasitic reaction was almost completely suppressed. At a discharge current density of 1.0 mA/cm², the Al-air cell achieved a capacity of 2507 mAh/g. The increase in KOH concentration and water content in the anolyte would decrease the capacity of Al. With increasing of KOH concentrations from 1 M to 4 M, the capacity densities decreased from 2507 mAh/g to 1330 mAh/g. While with increasing the water content from 0% to 20%, 40% and then 60%, the capacity densities dropped consecutively from 2507 mAh/g, 2146 mAh/g, 999 mAh/g to 663 mAh/g, respectively.

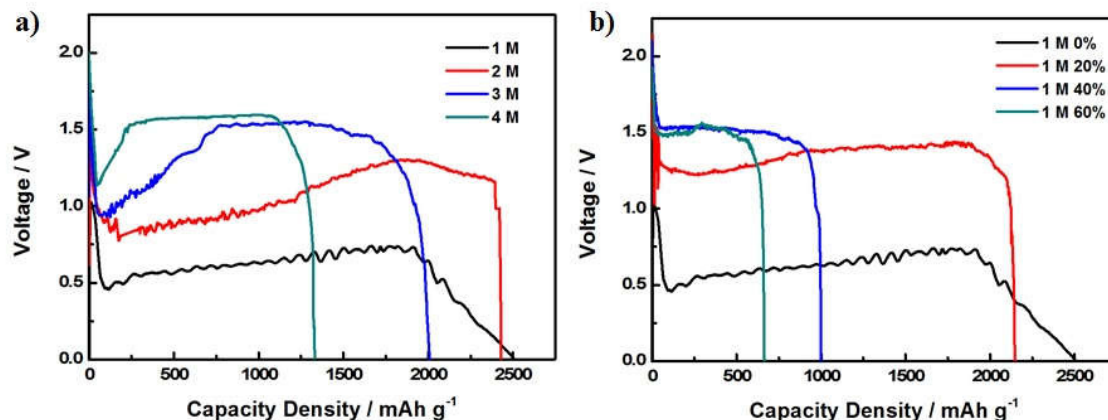


Figure 6 Capacity densities of the Al foil in Al-air cell with (a) KOH methanol-based anolyte of different concentrations and (b) 1 M KOH methanol-based anolyte containing different percentages of water.

4. Conclusions

The characteristics of a microfluidic Al-air cell working with a methanol-based anolyte are studied. The cell is built on a membraneless cell platform to avoid the use of the expensive membrane. The inhibition of crossover between different electrolytes was verified first to prove the operation feasibility of the cell. The influences of electrolyte concentration and water content were then investigated. The capacity tests show that the self-corrosion of Al can be effectively inhibited by the KOH methanol-based solution as anolyte. Under this operation, the Al-air cell achieved a high specific capacity density with low cost commercial Al foil.

Further work would be focused on investigating the reaction mechanism of Al in KOH methanol-based solution. Other tests such as impedance spectroscopy will also be conducted to characterize the electrochemical properties of this cell.

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Biography

Prof. Dennis Y.C. Leung received his Ph.D in 1988 from the Department of Mechanical Engineering at the University of Hong Kong. He joined the same department in 1993 and is now a full professor of the department specializing in renewable energy and energy conservation. He has published more than 400 articles including 210+ peer reviewed SCI journal papers. Prof. Leung is one of the top 1% highly cited scholars in energy field.