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A high specific capacity membraneless aluminum-air cell operated with an inorganic/organic hybrid electrolyte

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HIGHLIGHTS

- A concept of inorganic/organic hybrid electrolyte cell is demonstrated in Al-air cells.
- A non-direct counter-flow microfluidic platform is developed.
- High anodic specific capacity up to 2507 mAh g^{-1} is achieved.
- The reaction mechanisms of aluminum in methanol-based KOH anolyte are investigated.

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ABSTRACT

Aluminum-air cells have attracted a lot of interests because they have the highest volumetric capacity density in theory among the different metal-air systems. To overcome the self-discharge issue of aluminum, a microfluidic aluminum-air cell working with KOH methanol-based anolyte was developed in this work. A specific capacity up to 2507 mAh g^{-1} (that is, 84.1% of the theoretical value) was achieved experimentally. The KOH concentration and water content in the methanol-based anolyte were found to have direct influence on the cell performance. A possible mechanism of the aluminum reactions in KOH methanol-based electrolyte was proposed to explain the observed phenomenon.

1. Introduction

Cost-effective and high-density energy storage remains an unmet demand for applications ranging from portable electronics to large-scale grid storage. Metal-air cells represent one of the prospective candidates for fulfilling this demand, as they inherit the highest energy content of all known batteries by integrating inexhaustible ambient oxygen with anode metals that possess a high ratio of valence electron to atomic nuclei [1,2]. Among different anode metals, aluminum (Al) theoretically shows the highest volumetric capacity density (8.04 Ah m^{-3} vs. 2.06 for lithium, 3.83 for magnesium and 5.85 for zinc) and a high specific capacity (2.98 Ah g^{-1} vs. 3.86 for lithium, 2.20 for magnesium and 0.82 for zinc) second only to lithium, thereby explaining the attention it has attracted [3]. Further advantages of the aluminum-air (Al-air) cell over other metal-air technologies include the abundance of anode raw materials, ease of handling, and excellent safety characteristics [4]. However, early developments of Al-air cell have achieved little commercial success, mainly due to the dependence on the use of aqueous electrolytes, which suffered from severe self-discharge problems and resulted in practical energy densities inferior even to those of zinc-air systems [5]. An alternative idea of replacing the aqueous electrolytes with aprotic/organic ones has recently shown great promise by circumventing the conventional water-related problems, and has revived research activities on Al cells. Due to the low proton availability in the non-aqueous solvents, an almost complete inhibition of Al corrosion, and correspondingly, anode efficiency of nearly 100% have been demonstrated from half-cell experiments on the basis of methanol [6], ethanol [7], propanol [8], and ionic liquid electrolytes [9]. A big challenge, however,

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appears to be that most non-aqueous solvents will present difficulties when in contact with the air cathode, which has seriously impeded the progress of full-cell development. Typical issues at the cathode of a non-aqueous metal-air cell include electrolyte decomposition by peroxide radical attack or other parasitic reactions with the catalytic electrode [10], cathode clogging by insoluble products [11,12], and electrolyte contamination by absorbing ambient gases or moisture through the open structure of the gas diffusion cathode [13].

Non-aqueous/aqueous hybrid cell is an emerging technology that addresses the limitations of traditional single-electrolyte cell structures by operating electrodes in different electrolyte environments. The co-existence of both non-aqueous and aqueous solutions in a single cell is enabled with the incorporation of a solid layer made from materials such as LISICON [14], NASICON [15], and polymer [16]. The solid layer serves as both the membrane separator and the ion conductor between two different electrolytes. Feasibility of this concept has been successfully demonstrated in various prototypes, such as Li-air batteries [15,17], Li-NiOOH batteries [18,19], Li-AgO batteries, etc. [20]. Recent works have reported novel redox flow lithium batteries that employ an anolyte and a catholyte containing different redox mediators separated by a Nafion/PVDF membrane to achieve optimum performance [21,22]. However, practical operations of these hybrid systems have generally shown low performance and a short life span due to intrinsic drawbacks of the solid separator, including large ohmic resistance and poor chemical stability in strong alkaline or acidic environments [23].

To avoid the problems associated with the use of a solid separator, laminar flow-based microfluidic electrochemical cells have been extensively researched [24–26]. With a small ratio of inertial to viscous force, a laminar flow-based cell is able to maintain an interface between two streams of electrolytes, which acts as a virtual separator to prevent the mixing of different electrolytes within the cell [27]. Yet, because most organic solvents have a very high affinity to form mixtures with water, a new membraneless strategy needs to be developed for an inorganic/organic hybrid electrolyte system.

This work reports a novel inorganic/organic hybrid electrolyte design for Al-air cell to achieve high specific capacity. The design eliminates the need for a solid-state separator by relying on a non-direct counter-flow microfluidic platform. Methanol was applied as an organic electrolyte solvent at the anode side, which has been shown to be an effective corrosion inhibitor for Al anodes [6,28]. Traditional aqueous KOH electrolyte was applied at the cathode side. The interfacial mixing of the two electrolytes was visualized under different flow rates. The effects of KOH concentration and water content in the methanol-based anolyte on the cell performance were investigated. Post-discharge products of the cell were analyzed using XRD and FTIR, and reaction mechanisms in this newly-developed hybrid electrolyte cell were proposed. The cell design developed in this study can also be applicable to other metal-air systems.

2. Experimental

2.1. Chemicals

Alkaline electrolytes with different concentrations of KOH were prepared by dissolving KOH pellets (≥85%, Sigma-Aldrich, Hong Kong) in methanol (≥99.9%, Merck KGaA, Germany) and in 18 MΩ deionized water (Barnstead, NANOpure Diamond™, USA) under different test conditions. Commercial Al foil with an area density of 3.54 mg cm^{-2} was used as a cost-effective anode. The compositions of the foil were analyzed by energy-dispersive X-ray on a Hitachi S-4800 microscope to have 99.0% purity of Al with trace amounts of Fe and Ag as impurities. A gas diffusion electrode (GDE, Hesen Company, China) with a catalyst loading of 2 mg cm^{-2} Pt/C (Johnson Matthey, USA) was adopted as the air cathode for oxygen reduction.

2.2. Cell fabrication and assembly

The cell consisted 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 contained two inlets and one outlet for electrolyte flows. The two inlets were respectively connected to the anolyte sub-channel and catholyte sub-channel cut out on the second layer. On the third (bottom) layer, two square windows were cut out to allow the electrodes to contact with the electrolytes. The active projected electrode area was 0.015 cm^2, and all current and power densities were normalized by this area. The distance between the anode and the cathode was 2.0 mm. The three layers had thicknesses of 0.1 mm, 0.5 mm, and 0.1 mm, respectively, and they were bound together using double-side adhesive tape. The electrolyte was pumped into the cell by a syringe pump (LSP02-1B, LongerPump, China), via 1.5 mm tubing bonded to the ports with epoxy. Copper foil was used as a current collector to connect the electrodes to an external circuit.

2.3. Fluorescent dye characterization

Solutions of bromophenol blue ($C_{19}H_{10}O_5Br_4$), a methanol/water-ratio-sensitive dye, were prepared with a concentration of 1.75 mg mL^{-1} 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 a wavelength ranging between 600 and 630 nm. At this wavelength range, the methanol solution of $C_{19}H_{10}O_5Br_4$ is a transparent orange solution, while its water solution is opaque. The color is gradually transformed when the volume ratios of methanol/water changes. For calibration, the colors of $C_{19}H_{10}O_5Br_4$ solutions with different methanol/water volume ratios were captured by the Illuminator. Then, pure $C_{19}H_{10}O_5Br_4$ 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. Electrochemistry

Electrochemical measurements were conducted under room conditions. The polarization curves were obtained by potentiostatic current measurement at every 0.2 V for 200s to reach a steady state, from open-circuit voltage (OCV) to 0 V, by an electrochemical workstation (CHI 660E, Shanghai Chenhua Instruments Co., Ltd., China). The average value of the current data in the last 50 s of the sampling was used to represent the cell current at a certain voltage. An external Ag/AgCl (in saturated KCl) electrode (Shanghai Lei-ci Co., Ltd., China) was used as a reference electrode to acquire the single-electrode potentials of the cells. The potential data was recorded in situ by a digital multi-meter (15B, Fluke Corporation, USA). Electrochemical impedance spectroscopy (EIS) tests were taken in the frequency range of 120 kHz-5 mHz with an A.C. amplitude of 5 mV at 0.8 V, which was around the peak-power voltage.

To evaluate the specific capacity of Al in the cell discharged at a small current density, where Al suffers serious corrosion, galvanostatic discharging was performed at a current of 0.015 mA, corresponding to a current density of 1.0 mA cm^{-2}. The specific capacity (C) and Coulombic efficiency (η) of Al were calculated as: