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High-potential zinc–lead dioxide rechargeable cells

P.K. Leung, Q. Xu, T.S. Zhao*

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

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ABSTRACT

A zinc–lead dioxide rechargeable cell with an electrolyte composition of 1.5 mol dm^{-3} Zn(II), 0.5 mol dm^{-3} Na(I) and 0.3 mol dm^{-3} sulfuric acid is proposed and tested. The experimental results show that the open circuit potential of the zinc–lead dioxide cell is as high as 2.4 V (20% higher than conventional lead-acid cells and 56% higher than recent copper–lead dioxide cells), while the average coulombic and energy efficiencies are 90% and 70%, respectively, over 90 cycles at 20 mA cm^{-2}. Furthermore, it is shown that the measured specific energy of the zinc–lead dioxide cell in a stack configuration is about 30% larger than that of a commercial valve regulated lead acid cell at the same operating conditions.

1. Introduction

Due to the increasing demand of the efficient use of excess power generation and intermittent renewable sources, recent efforts have been focused on the development of low-cost, efficient and safe energy storage systems for large scale applications. Among different types of technology, aqueous rechargeable cells have attractive features in power output and safety properties. However, their cell potentials are often limited to less than 1.5 V due to the potential window of water electrolysis [1,2]. To-date, the lead acid cell remains one of the commonest aqueous systems as it has an open circuit potential as high as *c.a.* 2.05 V, which is attributed to the electro-positive nature of the lead dioxide reaction (+1.685 V *vs.* SHE) in acidic media [3–6]. Recently, several aqueous cells based on lead dioxide positive electrodes have been introduced [1,7–13]. For instance, Li et al. [1] proposed an alkaline–acid MH_x–PbO_2 cell based on two ion-exchange membranes that has a discharge cell potential of about 2.15 V at <10 mA cm^{-2}. Similar to many aqueous rechargeable cells, separators used in the MH_x–PbO_2 cell are often high-cost and cannot effectively prevent the crossover of the electrolytes.

In order to further increase the cell potential and maintain a simple design, a high potential zinc–lead dioxide rechargeable cell is proposed in this work. The proposed system is similar to the recent copper–lead dioxide cell [13] but uses zinc as the negative electrode to yield a high open circuit potential of *c.a.* 2.45 V. Due to the fact that lead (II) ion is almost insoluble in sulfuric acid (<6.5 mg dm^{-3} [14,15]), any electrodeposition associated with lead (II) ion is negligible; zinc electrodeposition is therefore the main primary reaction at the negative electrode. As a result, sulfation of the negative electrode can be avoided, which is often observed in conventional lead acid cells in the presence of sodium sulfate [16] or at low sulfuric acid concentration [17–20]. Hence, an electrolyte of lower acid concentration can be used to reduce the amount of hydrogen evolution during zinc electrodeposition on the carbon polymer substrate, leading to improved coulombic efficiency.

During charge, metallic zinc deposits at the negative electrode on a light-weight carbon polymer substrate (1.7 g cm^{-3}), while lead sulfate undergoes solid-phase transformation to form lead dioxide at the positive electrode. During discharge, these reactions are reversed as shown in the following equations:

At the negative electrode:

$$Zn^{2+}(aq) + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Zn(s) \quad -0.76\,V \quad vs.\ \ SHE \tag{1}$$

where hydrogen evolution can take place as a side reaction

$$2H^+(aq) + 2e^- \xrightarrow{\text{Charge}} H_2(g) \quad 0\,V \quad vs.\ \ SHE \tag{2}$$

At the positive electrode:

$$PbSO_4(s) + 2H_2O(aq) \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} PbO_2(s) + 2H^+(aq) + H_2SO_4(aq) + 2e^- \quad +1.685\,V \quad vs.\ \ SHE \tag{3}$$

while oxygen evolution can also take place:

$$H_2O(aq) \xrightarrow{\text{Charge}} 0.5O_2(g) + 2H^+(aq) + 2e^- \quad +1.23\,V \quad vs.\ \ SHE \tag{4}$$

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* Corresponding author. Tel.: +852 2358 8647.
E-mail address: metzhao@ust.hk (T.S. Zhao).

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The overall cell reaction is:

$$Zn^{2+}(aq) + PbSO_4(s) + 2H_2O(aq) \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Zn(s) + PbO_2(s) + 2H^+(aq) + H_2SO_4(aq) \quad c.a. \quad 2.45\,V \tag{5}$$

Together with the recent zinc–cerium rechargeable cell (2.3 V) [21–25], this cell offers one of the highest theoretical cell potentials in an aqueous electrolyte. Such a high cell potential is comparable to state-of-art lithium ion cells with enhanced safety property based on the $Li_4Ti_5O_{12}$ anode and the $LiFePO_4$ cathode (*c.a.* 1.2–2.4 V [26,27]). Despite the large specific energy of lithium-ion cells, their operating current densities are often lower than 5 mA cm^{-2} [28]. Hence, a large active area is needed for the equivalent power output, leading to a further increase in cost and complexity of the system. The concept of the zinc–lead dioxide rechargeable cell can be traced back to the 1970s in the descriptions of a few patents [29–31]. However, this system has not received much attention due to the large ohmic loss observed at low current density (<10 mA cm^{-2}) as reported by Abdo and Fahidy [32].

With the commercial lead dioxide positive electrode, we proved that zinc–lead dioxide cells can discharge at cell potential of *c.a.* 2.1 V and have a round-trip energy efficiency of *c.a.* 72% over 90 charge–discharge cycles at 20 mA cm^{-2}. Half-cell investigations were used to characterize the electrochemical behaviors of each electrode and define the optimum electrolyte compositions. The use of light-weight carbon polymer substrates enables the weight of a zinc–lead dioxide cell in a stack configuration to be about 26% lower than that of the commercial lead acid cells, in which more than 40% of the weight is attributed to lead or other lead alloy components [33,34].

2. Experimental

2.1. Chemicals and pretreatments of electrodes

Analytical grade zinc(II) sulfate heptahydrate powder (NaCalai Tesque, Inc., Japan, 99.0% purity), sodium sulfate powder (Sigma–Aldrich, USA), lead(II) nitrate powder (Sigma–Aldrich, USA), copper(II) sulfate powder (BDH Chemicals, UK) and reagent grade sulfuric acid (Merck KGaA, Germany) and nitric acid (VWR Int. LLC) were used. The metallic lead and lead dioxide electrode were extracted from a fully discharged commercial Yuasa NP 1.2-6 valve regulated lead acid cell (3× 2 V, 1200 mA h at 20 h rate) with three cells connected in series. In each cell, three metallic lead electrodes were sandwiched by two lead dioxide pastes with microglass fiber separators inserted between them. The active area per electrode was 7.6 cm^2 (2.75 cm × 2.75 cm), yielding a total active electrode area of 30.3 cm^2 in each single cell. The rated capacity per electrode area of the commercial lead acid cells used is about 39.6 mA h cm^{-2} (1200 mA h/30.3 cm^2) at 20-h discharge rate.

Prior to each experiment, metallic lead and lead dioxide electrodes extracted from the commercial cells were dipped in 30% (v/v) sulfuric acid for 20 s. Carbon polymer negative electrodes of 2 cm × 3 cm (TF6 bipolar, 0.6 mm, 1.3 g, 1.7 g cm^{-3}, SGL Carbon, Germany) for both zinc–lead dioxide and copper lead dioxide cells were pretreated by manually polishing its surface using silicon carbide paper grade P120, degreasing with a detergent, following by ultrasonic cleaning for 1 min and then rinsing with deionized water.

2.2. Cyclic voltammetry

Cyclic voltammetry measurements were carried out in a three-electrode set-up. Carbon polymer substrate (TF6 bipolar, SGL Carbon, Germany) and a thin lead dioxide film with exposed areas of 1 cm^2 (1 cm × 1 cm) were used as the working electrode. A thin lead dioxide film was pre-deposited onto a graphite substrate by applying a positive constant current density of 15 mA cm^{-2} (oxidation reaction) for 10 min in a solution containing 1 mol dm^{-3} lead(II) nitrate and 1 mol dm^{-3} nitric acid (68 wt%). Typical electrolyte composition for cyclic voltammetry was 30 × 10^{-3} mol dm^{-3} Zn(II), 0.5 mol dm^{-3} Na(I) and 0.3 mol dm^{-3} sulfuric acid, while platinum mesh (1 cm × 1 cm) was used as the counter electrode. A saturated Ag|AgCl reference electrode (ABB, Series 1400, sat'd KCl, Switzerland) was equipped with a liquid junction protection tube to avoid contamination from the sulfate medium and was placed at about 2 mm from the electrodes of interest. The electrochemical measurements were made with an EcoChemie Autolab (PGSTAT20) potentiostat (Netherlands), which was interfaced to computer using the General Purpose Electrochemical Software (GPES).

2.3. Charge–discharge experimental setup

For a typical test of a zinc–lead dioxide rechargeable cell, a 20 cm^3 electrolytes was prepared with 10.8 g $ZnSO_4{\cdot}7H_2O$, 4.0 g $Na_2SO_4{\cdot}10H_2O$, 0.4 cm^3 H_2SO_4 (97 wt%) and deionized water, which is equivalent to electrolyte compositions of 1.5 mol dm^{-3} Zn(II), 0.5 mol dm^{-3} Na(I) and 0.3 mol dm^{-3} H_2SO_4. The electrolytes were contained in a 25 cm^3 glass beaker (Fisher Scientific, UK), in which the negative and positive electrodes were placed with a distance of *c.a.* 1 cm from each other. A commercial carbon polymer electrode (TF6 bipolar, SGL Carbon, Germany) was used as the substrate for the zinc negative half-cell reaction, while positive electrode was a lead dioxide paste extracted from a fully discharged commercial valve regulated lead acid cell (Yuasa NP 1.2-6).

For cell performance comparison, a copper–lead dioxide cell was constructed in the same configuration but used 1 mol dm^{-3} $CuSO_4$ and 1.9 mol dm^{-3} H_2SO_4 as an electrolyte according to the reported work of Pan et al. [13]. Similar to this, a home-made lead-acid cell (flooded type) was made of negative lead and positive lead dioxide electrodes, which were extracted from the fully discharged commercial lead acid cells (Yuasa NP 1.2-6). The electrodes were about 1 cm away from each other and placed in a 25 cm^3 glass beaker (Fisher Scientific, UK) containing 4 mol dm^{-3} H_2SO_4 (*c.a.* 1.22 specific gravity).

During charge and discharge experiment in Section 3.3, the areas of all electrodes were ensured to be 4 cm^2 (2 cm × 2 cm) exposed to the electrolyte. In order to avoid overcharge and excessive gaseous evolutions, the cells were charged at constant current density of 20 mA cm^{-2} (80 mA) for 30 min and discharged down to 1.0 V at the same current density (20 mA cm^{-2}) at room temperature. The resulting capacity was 40 mA h (80 mA × 0.5 h), which is about 50% of the total discharge capacity at 20 mA cm^{-2} (77.3 mA h as determined in Section 3.3). The change in proton concentration ([H$^+$]) during charge–discharge processes were determined by titrating an aliquot of electrolyte solution (0.5 cm^3) with a 0.02 mol dm^{-3} NaOH solution using phenolphthalein (Sigma–Aldrich, USA) as a colorimetric indicator.

In Section 3.6, the zinc–lead dioxide cell in a stack configuration was tested using the design of commercial valve regulated lead acid cells (Yuasa NP 1.2-6, 1.2 Ah, 3× 2 V), in which three carbon polymer electrodes (TF6 bipolar, SGL Carbon, Germany) were used instead of metallic lead electrodes as in the commercial lead acid cells and were sandwiched by two positive lead dioxide pastes in monopolar connections. As the active area of each electrode is 7.6 cm^2 (2.75 cm × 2.75 cm), the total active area of the cell stack is 30.3 cm^2 (7.6 cm^2 × 4). The capacity of the resulting cells was measured by the procedures described in Section 2.4.