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A low-cost, high-performance zinc–hydrogen peroxide fuel cell

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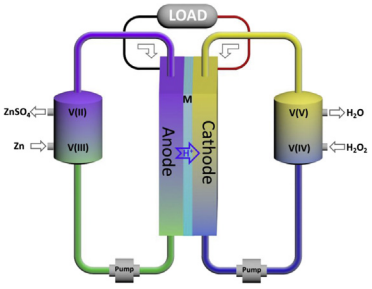
HIGHLIGHTS

- A catalyst-free, high-performance Zn $-H_2O_2$ fuel cell is proposed.
- It consists of a redox flow cell with redox ions regenerated by fuel/oxidant.
- It exhibits a peak power density of 1192 mW cm^{-2} at 60 °C.
- The performance is much higher than conventional cells with the same fuel/oxidant.

GRAPHICAL ABSTRACT



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ABSTRACT

Electric vehicles (EVs) are primarily limited by the distance they can travel, charge time and cost. Here we report a catalyst-free, high-performance zinc–hydrogen peroxide fuel cell that consists of a redox flow cell with the respective redox couple at the anode (V(II)/V(III)) and cathode (V(IV)/V(V)) regenerated by the fuel (zinc) and the oxidant (hydrogen peroxide). Unlike batteries that have low capacities and need to be frequently charged, the present fuel cell enables future vehicles to travel farther distances on one charge and almost instantaneous charge time. More importantly, it is demonstrated that this novel fuel cell exhibits an extraordinarily high peak power density of 1192 mW cm^{-2} at 60 °C, a performance which is about five times higher than that of state-of-the-art conventional fuel cells of the kind (265 mW cm^{-2}). Another striking feature of the present fuel cell is that it does not require catalysts, allowing the power pack to be both cost-effective and durable. These important features make the present fuel cell a promising post lithium-ion technology, opening a sustainable way to propel next-generation vehicles.

1. Introduction

Replacing petroleum with electric propulsion has been recognized as an effective means to decrease the strain on the environment [1]. Lithium-ion technology currently dominates the battery market of electric vehicles (EVs), but EVs have achieved little market penetration, primarily because of the high cost and low energy density of even state-of-the-art lithium-ion batteries [2]. An alternative energy-conversion technology, fuel cells, which convert chemical energy stored in a fuel directly into electrical energy, are expected to become a key enabling technology for powering EVs, due to its high energy density and comparatively short refueling time [3,4].

Fuel cells, which power EVs, typically use hydrogen as a fuel. This raises the issues of hydrogen production, transportation and storage, all while minimizing cost. Moreover, commercialization of hydrogen fueled fuel cells cannot be successfully achieved until safety issues resulting from the use of pressurized hydrogen are resolved, not to mention the high cost involved in the use of platinum catalysts required for electrochemical reactions [5,6].

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Alternative sources of fuel, such as zinc, have recently attracted increasing attention. Fuel cells which use zinc as fuel not only exhibit high energy density, but are also low in cost in comparison to hydrogen fueled cells, since only non-precious metal catalysts are required [7]. Zinc fueled fuel cells have, therefore, been recognized as a promising power source to propel EVs. Unfortunately, current state-of-the-art performance (265 mW cm^{-2}) of zinc-fueled fuel cells has not yet been able to meet requirements for practical applications in EVs [2].

In this work, we propose a catalyst-free, high-performance zinc–hydrogen peroxide fuel cell. This type of fuel cell consists of a redox flow cell with the respective redox couple at the anode and cathode regenerated by the fuel (zinc) and the oxidant (hydrogen peroxide), as shown in Fig. 1. The introduction of two redox couples to the conventional fuel cell system brings several striking features. First, the absence of catalysts makes the present fuel cell cost-effective. Second, the presence of redox couples significantly improves the electrochemical kinetics, thereby resulting in a high-performance fuel cell (1192 mW cm^{-2} at 60 °C). Finally, the sole use of carbon materials in preparing the electrodes makes this fuel cell durable.

2. Working principle

Fig. 1 illustrates the working principle of the present fuel cell system. Two redox couples, V(II)/V(III) and V(IV)/V(V), are used at the anode and the cathode, respectively. At the anode, the redox ions (V^{2+}) are oxidized by withdrawing electrons with the following ionic equation [8]:

$$V^{2+} \rightarrow V^{3+} + e^- \quad E_a^0 = -0.26V \text{ vs. SHE} \tag{1}$$

Released electrons pass through an external electrical load and arrive at the cathode. Protons migrate through the proton exchange membrane from the anode to the cathode. At the cathode, redox ions (VO_2^+) are reduced by receiving the released electrons [8]:

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \quad E_c^0 = 1.00V \text{ vs. SHE} \tag{2}$$

The discharge products, V^{3+} ions at the anode and VO^{2+} ions at the cathode, will be chemically charged (regenerated) by zinc and hydrogen peroxide in respective reactors according to:

$$\text{Reactor } \#1: \quad V^{3+} + {}^1\!/_2\, Zn \rightarrow V^{2+} + {}^1\!/_2 Zn^{2+} \tag{3}$$

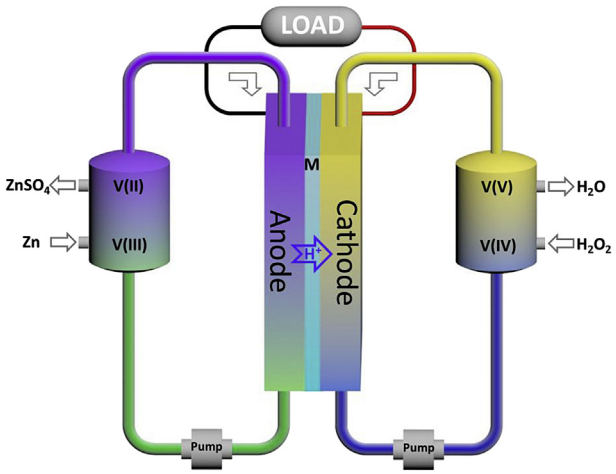

Fig. 1. Schematic of the zinc–hydrogen peroxide fuel cell system.

$$\text{Reactor } \#2: \quad VO^{2+} + {}^1\!/_2\, H_2O_2 \rightarrow VO_2^+ + H^+ \tag{4}$$

The combination of Eqs. (1)–(4) results in an overall reaction of this type of fuel cell:

$$Zn + 2H^+ + H_2O_2 \rightarrow Zn^{2+} + 2H_2O \tag{5}$$

3. Fuel-cell setup

In addition to a flow cell consisting of a membrane electrode assembly (MEA) sandwiched between two flow fields, the present fuel cell also includes two reactors for chemical charge, as shown in Fig. 1. The MEA, with an active area of 1.0 cm × 1.0 cm, was comprised of an as-received Nafion 212 membrane between an anode and a cathode [9]. Both the anode and cathode were made of three pieces of carbon paper (SGL: 10 AA) [10]. The two reactors are made of glass. The aqueous solutions containing 1.0 M vanadium ions (vanadium sulfate: ZhongTian Chemical Ltd., China) and 2.5 M sulfuric acid (Sigma–Aldrich) were fed to the flow cell by using a 2-channel peristaltic pump (WT-600-2J, Longerpump, China). The cell temperature was measured with a thermocouple located at the anode current collector, and two electrical heating rods were installed in the fixtures to control the operating temperature [11]. Polarization curves were measured by an electric load (Arbin BT2000) [12]. Potentiometric titration was conducted to examine the chemical charges of V(III) ions by zinc (Aldrich) and V(IV) ions by H_2O_2 (Honeywell), respectively. The potentials were measured by a voltmeter with a Pt mesh as working electrode and a saturated calomel electrode as reference electrode.

4. Results and discussion

4.1. Chemical charge

Fig. 2 shows the chemical charge processes of the vanadium ions by zinc and hydrogen peroxide, respectively. It can be seen from Fig. 2a that adding zinc powder into the aqueous solution, initially containing 1.0 M V(V) ions, changes the potential from 0.972 V to −0.460 V, meaning that zinc can successively reduce the V(V) ions to V(IV), V(III), finally V(II) ions. The potential change roughly from 0.0 V to −0.3 V indicates that the discharge products at the anode, V(III) ions, can be chemically charged to V(II) ions by zinc [13]. Similarly, it is seen from Fig. 2b that by feeding hydrogen peroxide, the potential of the aqueous solution, initially containing 1.0 M V(II) ions, changes from −0.420 V to 0.846 V, meaning that hydrogen peroxide can successively oxidize the V(II) ions to V(III), V(IV), finally V(V) ions. The potential change roughly from 0.4 V to 0.8 V indicates that the discharge product at the cathode, V(IV) ions, can be chemically charged to V(V) ions by hydrogen peroxide [14]. It should be noted that the two chemical reactions have very fast reaction rates and can be completed within a few seconds, indicating that the two chemical charge processes are not the limiting factor for the power output of this fuel cell.

4.2. Electrochemical discharge

Fig. 3 shows the polarization and power density curves of the zinc–hydrogen peroxide fuel cell at 60 °C. It is seen that the open-circuit voltage (OCV) and the peak power densities are 1.55 V and 1192 mW cm^{-2}, respectively. Recently, Li and Dai [15] developed a high-performance zinc fueled fuel cell based on hybrid electrocatalysts, resulting in an OCV of 1.40 V and a peak power density of 265 mW cm^{-2}. The peak power density achieved by the present fuel cell is about five times higher than the state-of-the-art