Short communication

A cerium–lead redox flow battery system employing supporting electrolyte of methanesulfonic acid

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HIGHLIGHTS

- A novel cerium–lead redox flow battery is developed and preliminary investigated.
- Excellent cycling performance of over 800 cycles was demonstrated.
- The battery could be operated over a broad temperature range.

GRAPHICAL ABSTRACT
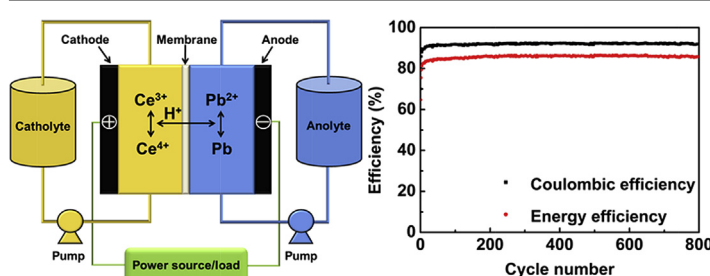
ARTICLE INFO

ABSTRACT

A novel cerium–lead redox flow battery (RFB) employing Ce(IV)/Ce(III) and Pb(II)/Pb redox couples in the supporting electrolyte of methanesulfonic acid (MSA) is developed and preliminarily investigated. The RFB requires no additional catalyst and uses kinetically favorable reactions between low-cost reactants, and provides a desirable discharge voltage of approximately 1.7 V, with high average coulombic efficiency (CE) of 92% and energy efficiency (EE) of 86% over 800 cycles at 298 K. Stable cycling with an acceptable performance is achieved for a board operating temperature range of 253 K–313 K. The excellent performance obtained from the preliminary study suggests that the cerium–lead RFB promises to be applicable to large-scale energy storage for electricity grids.
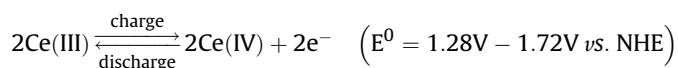
1. Introduction

Redox flow batteries (RFBs) serving the purpose of storing large-scale energy more economically and efficiently, are expected to circumvent the intermittent breakdown of renewable energy sources that affects the supply reliability of distributed generation systems [1,2]. Since the concept was first brought forth by Thaller in 1974 [3], a wide variety of RFB systems have been reported, such as the iron–chromium [4], all-vanadium [5–9], cerium–zinc [10–14], soluble lead-acid [15–18], and bromine-polysulfide [19]. The all-vanadium RFB which has been commercialized for various applications could be one of the most notable systems. Despite the significant advantages in commercialization, it still suffers from
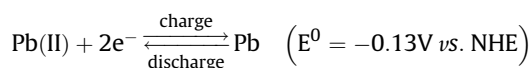
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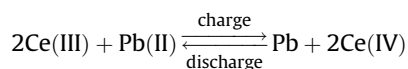E-mail address: lmwang@ciac.ac.cn (L. Wang).

some drawbacks such as high cost attributed to the costly vanadium electrolyte, and low standard open-circuit cell voltage (*c.a.* 1.26 V) leading to less power output and low energy density [20]. Recently, the relatively inexpensive cerium and lead have been considered as suitable alternative active elements for RFB applications [21]. The Ce(IV)/Ce(III) redox couple has been reported to be utilized in the positive half-cell of cerium–zinc and cerium–hydrogen systems [22] since it yields a large positive potential which lies between 1.28 V and 1.72 V *vs.* NHE depending on the supporting electrolytes [13,23], giving rise to a high cell voltage and therefore, a great energy storage capacity [21]. Furthermore, some previously reports have demonstrated that the kinetics of the Ce(IV)/Ce(III) couple in various media are quite rapid [24]. Unfortunately, the practical application of cerium–zinc RFBs is severely hindered by zinc dissolution and hydrogen evolution since zinc is an active material in acidic electrolytes. As to the cerium–hydrogen system, it inherently differs from the conventional RFBs in that the reactants are in the gas phase rather than the liquid phase. This characteristic enhances mass transfer with the increase of storage tank volume, and therefore hydrogen compression or novel hydrogen-storage materials are necessary [25]. Lead, showing a higher hydrogen evolution overpotential than zinc, has been considered as an effective corrosion inhibitor for the zinc half-cell in cerium–zinc RFBs [26]. In addition, Pletcher et al. propose a new kind of soluble lead-acid systems based on the electrode reactions of Pb(II) in methanesulfonic acid (MSA) and adopting Pb(II)/Pb and PbO$_2$/Pb(II) redox couples in the negative and positive half-cells, respectively. Although the kinetic of the Pb(II)/Pb couple is rapid, the battery offers a low energy efficiency (EE) only in the range of 55–65% [27], ascribed to the substantial overpotential associated with the deposition and dissolution of PbO$_2$ in the positive half-cell [15,18]. In this work, we present a novel cerium–lead RFB system which is composed of the Ce(IV)/Ce(III) couple in the positive half-cell substituting the PbO$_2$/Pb(II) couple of the soluble lead-acid system, and the Pb(II)/Pb couple in the negative hall-cell in an attempt to make effective use of benefits from both cerium–zinc and soluble lead-acid systems. MSA characterized by low corrosivity and good ionic conductivity is used as supporting electrolyte, in that it allows a high solubility for lead and cerium ions [26]. As for the positive half-cell, the primary electrode reaction is:

$$2Ce(III) \underset{discharge}{\overset{charge}{\rightleftharpoons}} 2Ce(IV) + 2e^- \quad \left(E^0 = 1.28V - 1.72V \ vs. \ NHE\right)$$

While in the negative half-cell:

$$Pb(II) + 2e^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} Pb \quad \left(E^0 = -0.13V \ vs. \ NHE\right)$$

The overall cell reaction is:

$$2Ce(III) + Pb(II) \underset{discharge}{\overset{charge}{\rightleftharpoons}} Pb + 2Ce(IV)$$

The results reveal that both the positive and negative electrode reactions exhibit excellent stability and kinetic reversibility, and the potential difference between the positive and negative half-cell is considerably large. These characteristics of the cerium–lead RFB enable discharge of energy at high efficiency and cell voltage for a broad temperature range and long-term cycling.

2. Experimental

All electrolytes were prepared with deionized water throughout

the experiments. The Ce(III) and Pb(II) electrolytes were prepared by separately dissolving Ce(III) carbonate (Aladdin, 99.9 wt.%) and Pb(II) oxide (Aladdin, 99.9 wt.%) in reagent grade aqueous MSA (Alfa Aesar, 70 vol.%) under magnetic agitation. In order to deoxygenate, the electrolytes were purged with nitrogen gas stream prior to the electrochemical experiments. Cyclic voltammetry (CV) was carried out in a three-electrode electrochemical cell with a graphite felt as the working electrode, a saturated Ag/AgCl electrode as the reference electrode and a large area graphite felt strip as the counter electrode. A VMP3 electrochemical workstation (Bio-Logic) was used to conduct the CV measurements. Charge/discharge performance of the battery was galvanostatically tested using a proof-of-concept static cell as shown schematically in Fig. 1 (actual test rig see Fig. S1, Supplementary data). Polypropylene (PP) was used as the main construction material as the highly oxidizing electrolytes were corrosive to most other materials of construction. The cell was constructed by two PP end plates and a couple of electrolyte frames (PP). Graphite felts with no catalysts were used as both positive and negative electrodes, which were inserted into the frames exposing an active surface area of 8 cm^2 (40 mm × 20 mm) to the electrolyte, and then tightly compressed onto the graphite current collectors. The negative and positive electrodes were separated by a commercially available low-cost cation-exchange membrane (GEFC-104, Golden Energy). Four silicone rubber gaskets were placed between the cell components to provide a good seal. Additionally, the negative half-cell compartment contained 15 mL of 1.5 M Pb(II) methanesulfonate in 1.0 M MSA while the positive half-cell compartment contained 15 mL of 1.0 M Ce(III) methanesulfonate in 1.0 M MSA. Unless otherwise stated, the battery operated with a fixed charge capacity of 40 mA h was charged at 5 mA cm^{-2} (40 mA) and then discharged at the same current density until the voltage dropped to 0.5 V at 298 K. All charge/discharge measurements were performed with a BTS battery test system (NEWWARE).

3. Results and discussion

Repetitive CVs (0.6 V–1.7 V *vs.* Ag/AgCl, 7 mV s^{-1}) recorded on the graphite felt electrode in the mixture of 0.05 M Ce(III) methanesulfonate and 1.0 M MSA, are shown in Fig. 2a. The anodic and cathodic peaks of Ce(IV)/Ce(III) couple are observed at 1.56 V and 1.33 V *vs.* Ag/AgCl. For the sweep range, a favorable feature is the absence of significant oxygen evolution current with the graphite felt electrode. As shown in Fig. 2b, repetitive CVs (−0.7 V–0.2 V *vs.* Ag/AgCl, 7 mV s^{-1}) performed on the graphite felt electrode in 0.05 M Pb(II) methanesulfonate with 1.0 M MSA illustrates two distinct current peaks at −0.66 V and −0.13 V *vs.* Ag/AgCl, corresponding to the electrodeposition of Pb(II) and dissolution of lead film, respectively. No significant hydrogen evolution current is observed due to the high hydrogen evolution potential of lead. By averaging the reduction and oxidation peak potentials, formal potentials for Ce(IV)/Ce(III) and Pb(II)/Pb redox couples are estimated to be 1.45 V and −0.40 V *vs.* Ag/AgCl, respectively. The large difference between their electrode potentials enables the battery offer a high cell voltage, which is a key parameter for a RFB to achieve a high EE. For both redox couples, the shapes of the anode and cathode peak are relatively symmetrical, and the ratios of anodic to cathodic peak currents are close to 1, which indicates the redox reaction of the both couples on graphite felt electrodes are quasi-reversible in the supporting electrolyte of MSA. Furthermore, compared to the 1st cycle, no significant variation is observed in the 10th cycle voltammogram, as shown in Fig. 2a and b. This suggests the electrochemically favorable reversibility and cycling stability of the electrode reaction for the two couples in MSA, probably due to the good stability, high conductivity and large surface-area of