A low-cost iron-cadmium redox flow battery for large-scale energy storage

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HIGHLIGHTS

- An iron-cadmium redox flow battery with a premixed Fe/Cd solution is developed.
- The energy efficiency of the Fe/Cd RFB reaches 80.2% at 120 mA cm^{-2}.
- The capacity retention of the battery is 99.87% per cycle during the cycle test.
- The battery has a low capital cost of \$108 kWh^{-1} for 8-h energy storage.

ABSTRACT

The redox flow battery (RFB) is one of the most promising large-scale energy storage technologies that offer a potential solution to the intermittency of renewable sources such as wind and solar. The prerequisite for widespread utilization of RFBs is low capital cost. In this work, an iron-cadmium redox flow battery (Fe/Cd RFB) with a premixed iron and cadmium solution is developed and tested. It is demonstrated that the coulombic efficiency and energy efficiency of the Fe/Cd RFB reach 98.7% and 80.2% at 120 mA cm^{-2}, respectively. The Fe/Cd RFB exhibits stable efficiencies with capacity retention of 99.87% per cycle during the cycle test. Moreover, the Fe/Cd RFB is estimated to have a low capital cost of \$108 kWh^{-1} for 8-h energy storage. Intrinsically low-cost active materials, high cell performance and excellent capacity retention equip the Fe/Cd RFB to be a promising solution for large-scale energy storage systems.

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1. Introduction

The ever-increasing utilization of intermittent renewable energy sources such as wind and solar energy raises an urgent need for large-scale energy storage systems to be able to provide an uninterrupted and reliable power supply [1–5]. The redox flow battery (RFB) is a promising large-scale energy storage technology due to its unique features including ease of scalability, intrinsic safety and long cycle life [6–8]. Various RFB systems that include all-V, Fe/Cr, Zn/Fe, Zn/Ce and all-Cu RFBs have been investigated over the past few decades [9–27]. One of the prerequisites for widespread commercialization of RFBs in the energy storage market is to establish low capital cost. Energy storage devices must be economically viable to be able to match existing grid-level storage technologies of pumped hydro and compressed air; the US

Department of Energy has set a system target of \$100 kWh^{-1} [11]. Current RFBs, however, are nowhere near the stringent target, largely owing to the high-cost of active materials and low cell performance. For instance, the most widely studied vanadium redox flow battery (VRFB) is estimated to have a system capital cost of \$325 kWh^{-1} [28].

The system cost of a RFB is mainly composed of the energy part (electrolyte) and power part (cells) [11,29]:

$$C_S \approx C_E + C_P = \frac{3600}{\varepsilon F V_d} \sum_i \frac{Q_i M_i}{n_i} + \frac{1}{I V_d t} \sum_j U_j \tag{1a}$$

$$V_d = V_{eq} - IR - \eta_{pos} - \eta_{neg} \tag{1b}$$

where C_S, C_E and C_P are the system, energy-part and power-part cost (\$ kWh^{-1}), respectively; Q and M are the active material cost (\$ kg^{-1}) and molecular mass of the active material (g mol^{-1}), respectively; U is the cost of cell materials including electrodes,
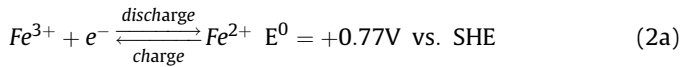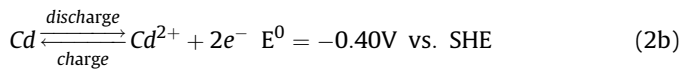
membranes and bipolar plates ($ m^{-2}); V_d and V_{eq} are the discharge cell voltage and equilibrium voltage (V), respectively; R is the internal resistance (Ω m^2); η is the activation loss (V); t is the designated discharge duration (h); and I is the operating current density (A m^{-2}). According to Eq. (1), a cost-effective RFB must have both inexpensive active materials as well as high cell performance, which is dictated by the kinetics of the active materials and conductivity of the supporting electrolyte.

As shown in Fig. 1, the iron-cadmium redox flow battery (Fe/Cd RFB) capitalizes on the redox couples of Fe(II)/Fe(III) and Cd/Cr(II) in the acid medium as the positive and negative electrolyte, respectively, which are separated by an ion-exchange membrane or a separator. The mechanism in which the Fe/Cd RFB stores and releases electricity can be expressed as follows:
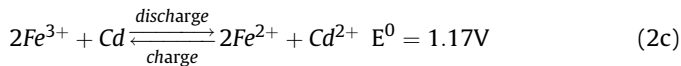
Positive electrode:

$$Fe^{3+} + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Fe^{2+} \quad E^0 = +0.77V \text{ vs. SHE} \quad (2a)$$

Negative electrode:

$$Cd \underset{charge}{\overset{discharge}{\rightleftharpoons}} Cd^{2+} + 2e^- \quad E^0 = -0.40V \text{ vs. SHE} \quad (2b)$$

Overall reaction:

$$2Fe^{3+} + Cd \underset{charge}{\overset{discharge}{\rightleftharpoons}} 2Fe^{2+} + Cd^{2+} \quad E^0 = 1.17V \quad (2c)$$

The active material cost for the Fe/Cd redox system is estimated to be as low as $10 kWh^{-1}, which provides a solid foundation to be a cost-effective energy storage system. For the positive side, the Fe(II)/Fe(III) redox couple has excellent kinetics with a kinetic constant as high as 8.6×10^{-2} cm s^{-1} in the acid medium [30], and it has been studied as the positive redox couple in H$_2$/Fe, Fe/Cr, Fe/V, Zn/Fe RFB systems [11,12,31,32]. For the negative electrode, the Cd/Cd(II) redox couple has fast kinetics with an exchange current density of 316.1 mA cm^{-2} [33], which has been investigated as the negative redox couple in the Cd/chloranil and Cd/PbO$_2$ single flow batteries [33,34]. Metallic cadmium has a high overpotential for hydrogen evolution reaction and can be efficiently deposited in the acid medium [34], which allows the use of highly conductive acid as supporting electrolyte. Moreover, the RFB is a closed electrochemical system, which allows for centralized management of active materials on a large scale, and facilitates the recycling of
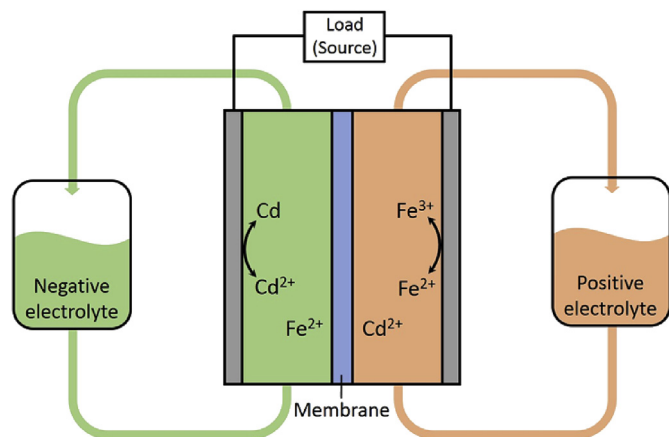
active materials. Thus, the use of cadmium in the closed large-scale RFB systems would not cause environmental issues [34].

In addition to low capital cost, the cyclic stability of a RFB is also of vital importance to reduce operating cost. An outstanding issue for the cyclic stability is cross-contamination when assembling a RFB using different elements as positive and negative redox couples, as the practical membranes are permeable not only to charge carriers (e.g., proton), but also to redox couples (Fe and Cd ions). The use of Fe and Cd ions at the positive and negative electrode, respectively, creates a large concentration difference through the membrane for the respective ion, resulting in a natural tendency for species crossover and capacity loss during operation. Re-separating Fe and Cd ions from the contaminated electrolyte will significantly increase operating cost and require accessory equipment. To tackle the cross-contamination issue, the identical mixed-reactant solution containing premixed iron and cadmium salts (e.g., 1.0 M Fe^{2+} + 0.5 M Cd^{2+}) is proposed for both the positive and negative electrolytes of 0% state-of-charge (SOC) in the Fe/Cd RFB. With the mixed-reactant solution, the capacity loss caused by the species crossover can simply recovers through re-mixing and re-separating the positive and negative electrolytes [32,35—37]. In this work, an iron-cadmium redox flow battery with a premixed iron and cadmium solution is developed and tested. The influence of acid composition on electrolyte stability has been investigated, and the capital cost of the Fe/Cd RFB is analyzed.

2. Experimental

2.1. Static cell

Static cell: The electrodes were fabricated with carbon paper (SGL, 10AA, 0.4 mm thickness) and pretreated in air at 500 °C for 5 h to increase wettability. Both negative and positive electrodes were composed of three layers of carbon paper with an active area of 1.0 cm × 1.0 cm, which were separated by a Nafion® NR-212 membrane. The 1.0 mm-thickness polytetrafluoroethylene gaskets were used. The graphite plates were installed as the current collectors, and were clamped by the aluminum endplates. For the Fe/Cd static cell with separate reactant, 80 μL solution of 0.3 M FeCl$_2$ (Aladdin) + 3.0 M HCl (VWR) and 80 μL solution of 0.15 M CdSO$_4$ (Merck) + 3.0 M HCl were used as the positive and negative electrolyte, respectively. For the Fe/Cd static cell with mixed reactant, 80 μL mixed-reactant solutions of 0.3 M FeCl$_2$ + 0.15 M CdSO$_4$ + 3.0 M HCl were used as the positive and negative electrolyte, respectively. The cycle tests of the static cells were conducted on Arbin BT2000 (Arbin® Instrument) at 15 mA cm^{-2} with a voltage window of 0.7—1.35 V.

2.2. Flow cell

Flow cell (redox flow battery): The zero-gap flow-through cell structure was used in the flow cell test. The flow cavities were machined on the graphite plates. The graphite felt electrode (SGL, 3.0 mm thickness) with an active area of 2.0 cm × 2.5 cm served as both the negative and positive electrodes, which were filled in the flow cavities and separated by a Nafion® NR-212 membrane. Polytetrafluoroethylene gaskets were used to give an electrode compression ratio of approximately 20%. The gold-coated copper current collectors were placed adjacent to the graphite plates, and were clamped by the aluminum endplates. 20 mL mixed-reactant solutions of 1.0 M FeCl$_2$ + 0.5 M CdSO$_4$ + 3.0 M HCl were used as the positive and negative electrolyte, respectively. The electrolytes were circulated in the Norprene® #16 Chemical Tubing by a 2-channel peristaltic pump (Longer pump, WT600-2J). The charge-discharge tests of the flow cell were conducted on Arbin BT2000

Fig. 1. Schematic of an iron-cadmium redox flow battery with a premixed iron and cadmium solution.