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A Sn-Fe flow battery with excellent rate and cycle performance

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HIGHLIGHTS

- A novel redox flow battery using iron and tin redox materials was presented.
- The energy efficiency of the battery was as high as 78.5% at 200 mA cm^{-2}.
- The battery can operate stably over 700 cycles at 200 mA cm^{-2}.
- The characteristic of tin deposition inside the porous electrode was disclosed.

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ABSTRACT

Hybrid flow batteries are one of the most promising technologies for storing the electricity generated from intermittent renewables, such as wind and solar. However, most of the existing hybrid systems currently suffer from low power density and poor cycle performance resulted from the parasitic reactions. To mitigate these issues, here we report a tin-iron hybrid flow battery in which the stannous chloride anolyte is separated from the ferric/ferrous chloride catholyte. With the reversible tin metal deposition/stripping and ferric/ferrous chloride redox reactions at carbon surfaces, the present battery delivers an energy efficiency of 78.5% even at the current density of 200 mA cm^{-2}. In addition, owing to high hydrogen overvoltage of metallic tin, the parasitic hydrogen evolution reaction in the negative electrode can be largely avoided so that the battery can stably operate over 700 cycles without obvious efficiency decay. With the excellent rate and cycle performance, it is envisioned that the tin-iron flow battery is a promising candidate for large-scale energy storage applications.

1. Introduction

Penetration of intermittent renewable energy, such as solar and wind, is now driving demand for large-scale energy storage systems (EESs) to resolve the mismatch problem existing between the intermittent electricity generation and variable consumption at multiple time-scales [1]. Among the large-scale EESs, redox flow batteries (RFBs) are receiving wide attentions due to the unique flow-cell architecture and advantages, including excellent scalability, high energy efficiency, long life time as well as high safety [2–4].

Basically, the RFBs can be categorized into all-liquid flow batteries and hybrid flow batteries. The first all-liquid flow battery invented by NASA employed Fe^{2+}/Fe^{3+} and Cr^{2+}/Cr^{3+} as redox couples, offering a standard voltage of 1.18 V. Although Fe^{2+}/Fe^{3+} redox couple exhibits a pretty good reversibility and fast kinetics at the carbon surfaces, issues associated with the aging of $CrCl_3$ and the severe hydrogen evolution at the negative electrode lead to a relatively poor cycle performance [5]. Different from Cr^{2+}/Cr^{3+} redox couple, V^{2+}/V^{3+} redox couple has an adequate potential of −0.23 V, largely mitigating the hydrogen evolution issue. Combining V^{2+}/V^{3+} and VO^{2+}/VO_2^{+} redox couples, Skyllas-Kazacos and co-workers developed the all-vanadium redox flow battery (VRFB), having the advantages of adequate cell voltage as well as elimination of cross-contamination [6–8]. Despite its compelling merits, the commercialization of VRFB is significantly hindered by the high capital costs of the precious redox-active materials and component materials. To address this issue, Aziz and co-workers developed and pioneered quinone-based organic flow batteries, aiming at cutting down the RFB cost by using organic redox active materials. The quinone-bromine and alkaline quinone flow batteries deliver decent power and cycle performance but the energy densities of these systems are still quite limited [9–14]. More detailed advances in organic flow battery can be found in the related review paper [15].

Although the idea of using organic species as redox couples opens up opportunities for aqueous RFB development, finding new redox

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couples to build a full liquid flow battery is still challenging since the redox couples are requested to simultaneously satisfy strict requirements of meaningful voltage, decent solubility, fast kinetics and low cost. Hence, hybrid RFBs, such as zinc-bromine, all-iron, and all copper flow batteries, have also been widely explored for large-scale energy storage applications [16–40]. Leung et al. developed a Zn-Ce flow battery and an energy efficiency of 46.8% was achieved at 20 mA cm^{-2} [16]. Wang and co-workers proposed a zinc-polyiodide flow battery and demonstrated a high energy density [18]. Yan et al. presented a double-membrane based zinc-iron flow battery and an energy efficiency of 76% was achieved at 80 mA cm^{-2} [22]. Recently, Zhang and co-workers developed a neutral zinc-iron flow battery with a low-cost porous membrane, significantly lowering the system capital cost [28]. Robert and co-workers developed an all-iron flow battery based on the slurry electrodes, demonstrating a voltage efficiency of 50% at 75 mA cm^{-2} [35]. Yu and co-workers proposed a low-cost, high-energy Fe-Al hybrid liquid battery and an energy density of as high as 166 Wh L^{-1} was successfully demonstrated [39]. Although significant progress has been made in development of hybrid flow battery systems, most of the hybrid systems suffer from poor rate performance (< 100 mA cm^{-2}) and short cycle life, which may be attributed to the sluggish kinetics, severe parasitic reactions as well as the metal dendrite formation during electroplating.

In this sense, building a hybrid flow battery with high rate capability and long life time is vitally important. To achieve such a goal, identifying metallic anode with fast kinetics and high hydrogen overvoltage is critical. Tin metal, which has been widely used in food industry to fabricate tin cans due to its low toxicity, possesses fast kinetics and high hydrogen overvoltage, offering a potential of -0.13 V (versus SHE) [41]. Hence, tin may be one of the ideal options as the anode materials. Besides, ferric/ferrous chloride redox couple, which has been adopted in different flow battery systems, is quite attractive as active material at the positive side due to its low cost and fast kinetics [42–46]. In this work, we propose a tin-iron hybrid flow battery in which the stannous chloride anolyte is separated from the ferric/ferrous chloride catholyte, as shown in Fig. 1. The electrochemical reactions can be depicted as follows:

$$\text{Negative side: } \frac{1}{2}Sn \leftrightarrow \frac{1}{2}Sn^{2+} + e^{-} \quad (E^{0} = -0.13\text{ V } vs.\text{ SHE})\mathbb{F} \tag{1a}$$

$$\text{Positive side: } Fe^{3+} + e^{-} \leftrightarrow Fe^{2+} \quad (E^{0} = 0.77\text{ V } vs.\text{ SHE}) \tag{1b}$$

$$\text{Overall: } Fe^{3+} + \frac{1}{2}Sn \leftrightarrow Fe^{2+} + \frac{1}{2}Sn^{2+} \quad (E^{0} = 0.9\text{ V }) \tag{1c}$$

During charge, metallic tin is electroplated onto the negative electrode from electrolyte while ferrous chloride is oxidized to ferric chloride at the positive electrode. Reverse reactions take place at corresponding electrode surface during the discharge process. As disclosed by the experimental results, with the reversible tin metal deposition/stripping and ferric/ferrous chloride redox reactions at carbon surfaces, the present battery demonstrates energy efficiencies ranging from 78.5% to 93.4% at the current densities of 40–200 mA cm^{-2}. In addition, excellent cyclic stability of the Sn-Fe flow battery can be also observed in the long-term cycling test. The excellent rate and cycle performance make the tin-iron flow battery embrace the large-scale energy storage applications.

2. Experimental

2.1. Preparation of the lab-scale Sn-Fe flow cells

The negative electrolytes with different concentrations were prepared by dissolving stannous chloride salts in hydrochloric acid while the ferrous chloride salts were dissolved into hydrochloric acid to form the positive electrolytes. The salts and acids were bought from ALADDIN Chemical Co., Ltd.. A single flow cell with serpentine flow fields at both positive and negative sides was assembled for the flow cell test. In the Sn-Fe flow battery, the reaction occurring in the negative electrode involves metal deposition/stripping while the reaction in the positive electrode involves no phase-change reaction. More space should be provided for metal deposition by the negative porous electrode, as compared to the positive porous electrode. In this sense, we used the carbon felt (Q-Carbon Material Co., Ltd.) with a porosity of 0.93 as the negative electrode and two layers of carbon cloths (ELAT® hydrophilic plain) with a porosity of 0.8 as the positive electrode. It should be noted that an additional non-conductive preoxidated felt was used to keep the space between the membrane and negative electrode to provide more space for tin deposition. To enhance the hydrophilicity and reaction kinetics, we thermally treated both electrodes at 500 °C for 5 h under air atmosphere. The active electrode area in this study was 4 cm^2 and the original thicknesses of the carbon felt, non-conductive preoxidated felt and carbon cloth (two layers) were 2.4 mm, 2.4 mm and 0.812 mm, respectively. The compression ratio for both electrodes was kept about 60%.

2.2. Flow cell test

The rate and cycling performance of the Sn-Fe flow cell were measured by the potentiostat/galvanostat (Arbin BT2000, USA). The cell was operated under a constant current with current densities ranging from 40 to 240 mA cm^{-2} and the upper and lower cut-off voltages were set as 0.4 and 1.26 V, respectively. Two solutions (0.5 M $SnCl_2$ + 3.0 M HCl and 1.0 M $FeCl_2$ + 3.0 M HCl) were used as the negative and positive electrolytes for the charge-discharge test, respectively. In both positive and negative sides of the battery, 25 μL of electrolytes were pumped by the two-channel peristaltic pump

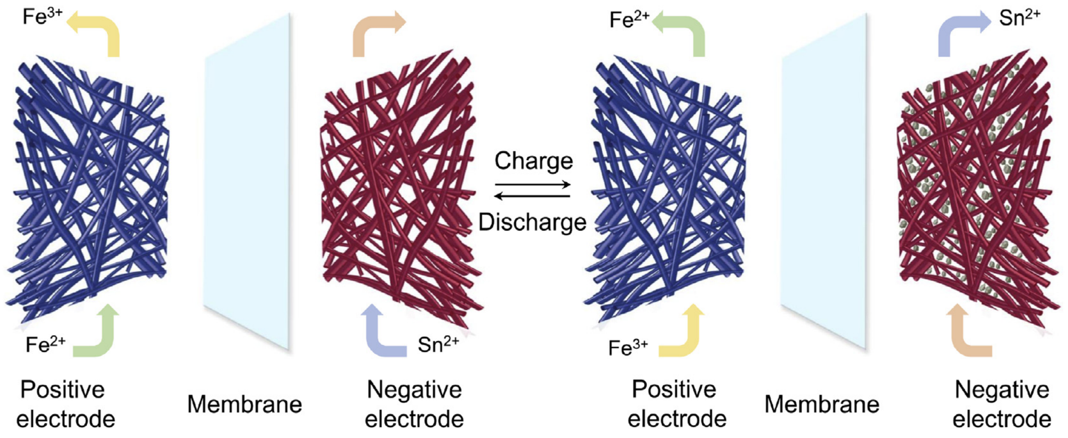

Fig. 1. Schematic of the working principle of the Sn-Fe flow battery.