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Short communication

Investigation on the performance evaluation method of flow batteries

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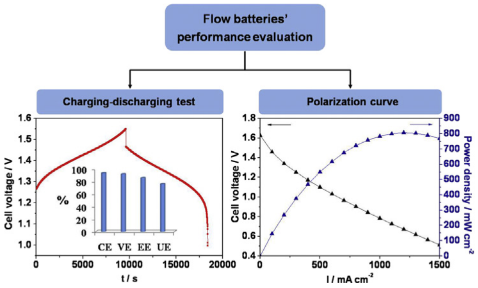
HIGHLIGHTS

- A proper performance evaluation method for flow batteries is very important.
- Polarization curve is not advisable to evaluate flow batteries' performance.
- Charging–discharging test is optimal for flow batteries' performance evaluation.

GRAPHICAL ABSTRACT



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ABSTRACT

Performance evaluation method is very important for the research on flow batteries. Charging–discharging test is the most typical evaluation method for flow batteries. Recently, the polarization curves, together with the associated power density curves, which are commonly employed in fuel cells, have come into use for flow batteries' performance evaluation. Based on the investigation of performance evaluation method, it is confirmed charging–discharging test is optimal for flow batteries' performance evaluation. A comparison of voltage losses (voltage efficiency, VE) can be clearly delivered from the polarization curves, which are quite practical for fuel cells' performance evaluation. While for flow batteries, apart from VE, coulombic efficiency (CE), energy efficiency (EE), utilization of electrolyte (UE) and capacity stability should be seriously considered during charging–discharging process. However, CE and UE are inaccessible; accordingly EE and capacity stability can't be detected from polarization curves. Therefore, the polarization curve is improper to serve as a performance evaluation method for flow batteries. On the premise of a proper CE, a rough performance evaluation for flow batteries can be achieved via the polarization curves. The peak power density is of limited significance in practical use due to the extremely low EE obtained at that point.

1. Introduction

Flow batteries are considered among the most promising technologies for large-scale energy storage due to their attractive features like long cycle life, high efficiency and high reliability [1–3]. A large number of flow batteries have been successively proposed and developed, such as all-vanadium [4], iron–chromium [5], bromine–polysulfide [6] and zinc–bromine [7]. Meanwhile, some relevant experimental and modeling studies have been performed to improve the battery performance through material innovation and structure optimization [8–15]. Therefore to achieve the reliable and comparable battery performance is essential, and a

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proper performance evaluation method for flow batteries is of great importance.

Currently, the most typical and commonly used performance evaluation method for flow batteries is charging–discharging test, mainly indicating four characteristics: (1) Coulombic efficiency (CE), the ratio of the average discharging capacity to the average charging capacity, (2) Voltage efficiency (VE), the ratio of the average discharging voltage to the average charging voltage, (3) Energy efficiency (EE), the ratio of the average discharging energy to the average charging energy, (4) Utilization of electrolyte (UE), the ratio of the actual discharging capacity to the theoretical discharging capacity. In addition, capacity fading, evaluated by plotting UE with respect to cycle number, is an indicator of capacity stability of flow batteries during charging–discharging cycling.

The polarization curves and the associated power density curves, which were widely used for performance evaluation of fuel cells [16,17], have recently come into use for flow batteries' performance evaluation [18–22]. The battery performance was improved via lowering the polarization and enhancing the peak power density by using this method. The polarization curves describe the output voltage at the specified current density, by which the mechanism of voltage losses can be extensively studied and the detailed research has been reported in Ref. [23]. And the power density curves are derived from the product of the output voltage and the corresponding current density.

Different from fuel cells, the flow batteries are rechargeable, where the overall performance is closely related to the charging–discharging process. However, the polarization curves can only identify the mechanism of the voltage losses; therefore it is necessary to access the availability of this method for performance evaluation and to clarify the issues that the polarization curves could address for flow batteries.

In this communication, membranes with different thicknesses were selected to further tune the internal resistance of batteries. The charging–discharging test and the polarization curves were presented respectively to evaluate the performance of flow batteries with different internal resistances. The performance consistence between the two methods was investigated. The feasibility of using polarization curves for flow batteries' performance evaluation was discussed.

2. Experimental

2.1. Battery construction and electrolyte system

As shown in Fig. 1, a vanadium flow battery (VFB), comprised of a membrane, electrodes (installed in the frames), frames and current collectors, was assembled for battery performance evaluation. Nafion-series with different thickness were used as membranes, including Nafion 115 (125 μm), 212 (50 μm) and 211 (25 μm) (Ion-Power, Inc.). The electrodes were carbon felts with an original thickness of 1 mm and a geometric surface area of 6.72 cm^2. Seals with a hollow area of 6.72 cm^2 served as the frames, where the electrodes were installed. The frames filled with electrodes and the membrane, were mounted by sandwiching between current collectors (graphite plates). The battery was assembled with gaskets suitable to compress the electrode material to a rough 80% of its original thickness. 40 mL of a solution containing 1.5 M VO^{2+}, 3 M H_2SO_4 and 40 mL of a solution containing 1.5 M V^{3+}, 3 M H_2SO_4 were used as positive and negative electrolyte, respectively.

2.2. Battery measurements

The charging–discharging test was conducted by an Arbin 2000 instrument at the current density ranging from 80 mA cm^{-2} to 200 mA cm^{-2}. The polarization curve was generally measured by controlled current-steady steps using a FC Impedance Meter (KFM 2030) with a maximum current of 30 A. A steady current below 2 mA cm^{-2} at a charging voltage of 1.75 V was taken to indicate 'fully charged' state of the electrolyte, consisting of V^{2+} on the negative side and V^{5+} on the positive side. The discharging polarization curve, started with the battery at 'fully charged' state, was studied. The battery was discharged at the specified current density for 30 s and then allowed to rest for up to a steady state at its open circuit voltage (OCV). The internal resistance (IR) of the battery was measured during the polarization curve test at 'fully charged' state by the aforementioned FC Impedance Meter.

All experiments were performed at room temperature (25 °C). Two centrifugal pumps were used to deliver electrolytes through the battery at a constant flow rate of 15 mL min^{-1}. A PTFE sealing component was sealed onto the negative reservoir to avoid oxidation of V^{2+}. The cutoff voltage for charging–discharging test was set at 1.55 V and 1 V to avoid the corrosion of carbon felt and graphite plate.

3. Results and discussion

3.1. Charging–discharging performance

A typical plot of charging–discharging voltage versus time is shown in Fig. 2, which is a fundamental description on the battery performance during charging–discharging process. Referring to Fig. 2(a), a raise in charging voltage and a decline in discharging

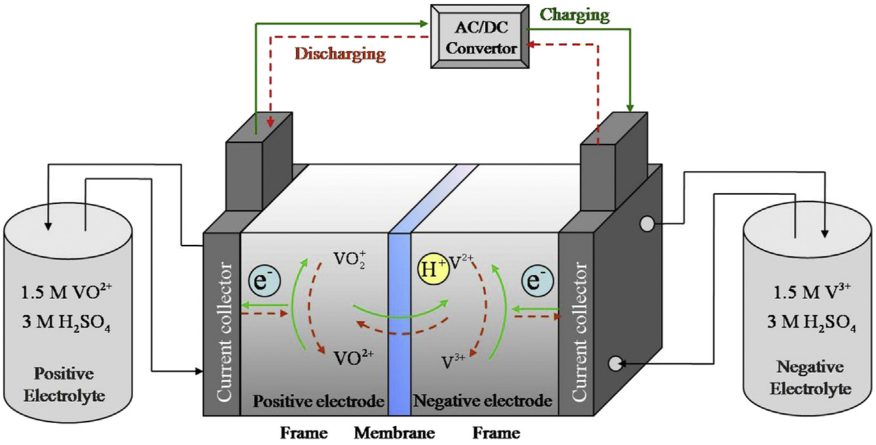

Fig. 1. Scheme of battery construction.