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A novel ultrasonic velocity sensing approach to monitoring state of charge of vanadium redox flow battery

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HIGHLIGHTS

- This is the first to apply ultrasonic sensing technique to monitor SOC of VRB.
- Ultrasound velocity is affected by concentration and temperature of a solution.
- The ultrasonic sensing is applicable to both positive and negative sides of VRB.
- An empirical model equation fits the results of this two-component system well.
- The SOC of a VRB can be properly measured using ultrasonic sensing.

ARTICLE INFO

ABSTRACT

A novel ultrasonic velocity sensing approach is proposed and investigated to monitor the state of charge (SOC) of a vanadium redox flow battery (VRB, or VRFB). The positive electrode is designated as the energy storage capacity-limiting one so that the molar ratio of the V^{5+} ion in the positive electrolyte solution determines the SOC of a VRB. The tested single-cell VRB is connected to an ultrasonic sensor and charged/discharged almost to its two extremes at a constant current of 2 A under various operating temperatures. It is found that the ultrasound velocity exhibits distinct variations in accordance with changes of vanadium ion compositions in the positive electrolyte solution as the SOC of the VRB varies. The SOC obtained can be depicted in a 3D plot in terms of ultrasound velocity and operating temperature. An empirical model equation is proposed and found to fit the experimental results of both charging and discharging stages quite well. The advantages of this SOC sensing approach are that it is totally independent of VRB operations and can be readily applied to both sides of the electrodes. It is expected to develop into a dependable method for accurate and real-time monitoring of SOC for VRB.
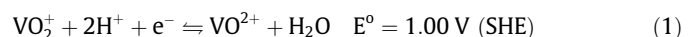
1. Introduction

Among a variety of energy storage systems, vanadium redox flow battery (VRB) has many technical advantages, such as long life cycle, minimal safety issues, high energy efficiency and excellent flexibility to scale up to the desired storage capacity. It is expected to become an attractive energy storage technology when medium- and large-scale storage applications of renewable energy, e.g., solar energy and wind power, and smart grid applications are desired [1,2]. The development of vanadium redox flow battery has been thoroughly described in several good review papers [2–6]. Its key operational conditions including the use of various kinds of modi-
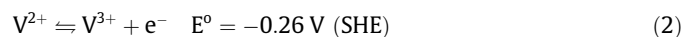
fications on battery cells [7–9] as well as modelling of VRB stacks and systems [10–12] have also been substantially reported.

Briefly, it is composed of a VO_2^+/VO^{2+} (or simplified as V^{5+}/V^{4+}) ion couple-based positive electrode and a V^{2+}/V^{3+} ion couple-based negative electrode with its vanadium ions commonly prepared in a suitable sulfuric acid aqueous solution. During charging/discharging operations, the electrolyte solutions are separately circulated through the two half-cell compartments, separated by a piece of proton exchange membrane (PEM). The reactions of a VRB can be represented as follows [13]:
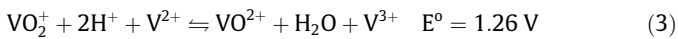
Positive electrode

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \quad E^o = 1.00\ V\ (SHE) \tag{1}$$

Negative electrode

$$V^{2+} \rightleftharpoons V^{3+} + e^- \quad E^o = -0.26\ V\ (SHE) \tag{2}$$

Overall cell reaction

$$VO_2^+ + 2H^+ + V^{2+} \leftrightharpoons VO^{2+} + H_2O + V^{3+} \quad E^o = 1.26 \text{ V} \tag{3}$$

The forward reaction stands for the discharging process and the backward reaction for the charging process of the VRB. The characteristics of vanadium redox flow batteries are their very rapid responses to changing loads and extremely large overload capacities. In addition, the VRBs can be deep discharged with low degradation rates, high roundtrip efficiencies and long lifetimes.

In general, the SOC of a VRB is determined by the molar ratio of its storage capacity-determining electro-active ion remaining in the negative or positive electrolyte solution. Therefore, the SOC of a VRB can be expressed as [14]

$$SOC = \frac{[V^{2+}]}{[V^{2+}] + [V^{3+}]} = \frac{[V^{5+}]}{[V^{4+}] + [V^{5+}]} = X \tag{4}$$

However, the all-vanadium system is susceptible to several mechanisms of capacity loss that are asymmetric, i.e. that affect one of the electrolyte solutions disproportionately. The vanadium electrolyte systems may lose capacity by becoming imbalanced, such that the reduced capacity of one of the electrolyte reservoirs dominates the battery performance. In the case of an electrolyte imbalance, the equality in Eq. (4) no longer holds. Thus, an ideal SOC measurement should be capable of sensing the state of charge of the electrolytes individually, so that the onset of imbalance can be detected [14].

In fact, SOC monitoring is a key issue for management of VRB operation. In addition to keeping away from imbalanced electrolyte conditions [15], as an integral part of the VRB operation, one would like to avoid pushing the charging/discharging conditions to overly exceed the extreme limits of its SOC. This can prevent excessive occurrences of undesirable side reactions and deterioration of VRB materials, so as to maintain long service life and high energy efficiency. The SOC-dependent electrolyte viscosity is also reported to affect the performance of a VRB [16]. Therefore, an accurate, simple and reliable method to monitor its state of charge is highly desirable for safe operation of such a promising energy-storage device. Recently, several techniques have been investigated to measure the SOC of a VRB, including conductivity, UV–vis absorption, open-circuit voltage (OCV), extended Kalman filter, potentiometric titration, and four-pole cell methods [17–20].

Among them, the OCV approach is the most commonly used method. Generally, a dummy cell is required, which is attached to the working VRB cells while the OCV is measured. The Nernst equation is applied to relate the measured OCV with the SOC of the VRB as [14]:

$$E = E^o + \frac{RT}{F} \ln \left[\frac{SOC^2 \cdot (c_{H^+} + SOC)^2}{(1 - SOC)^2} \right] \tag{5}$$

where E^o is the standard potential for the VRB (1.26 V), SOC is the molar ratio of the capacity-limiting species, and c_{H^+} is the initial proton concentration in the electrolyte. However, discrepancy between models and experiments [18] is encountered which is a severe drawback. In general, the most fitted range of SOC is only about 20–80%. Another drawback is that this method can only measure the SOC of the overall VRB and cannot monitor that of the positive or negative side separately as desired, which is unable to solve the electrolyte solution imbalance problem leading to poor efficiency in operation of VRB. More rapid, accurate and simple methods that can be applied to real-time measurements for on-line control [21] of the SOC of a VRB in both sides are desperately needed.

The variation of ultrasound velocity in an aqueous solution is a thermodynamic phenomenon [22]. Such acoustic variation can be affected by the system temperature and the concentrations of species existing in the solution. Recently, the ultrasonic velocity sensing technique has been applied to a variety of practical applications [23–25], particularly for sensing species concentrations in liquid environments. In the field of energy technology systems, of special interest is the sensing of methanol concentration in the fuel solution of a direct methanol fuel cell (DMFC) [26,27]. It was reported that the concentration of methanol can be correctly determined using an ultrasound detector, and the ultrasound velocity is strongly dependent on the temperature and concentration of the solution. In addition, the empirical "Impedance Dependence Relation (IDR)" equation [28,29] has been employed for dealing with a two-component mixture system, which assumes that the linearity and additivity of the ultrasound velocity exist with respect to molar ratios of acoustic impedances and densities of electrolyte solutions.

More recently, Steingart and coworkers [30,31] had reported using ultrasound for monitoring the SOC of Li-ion and alkaline batteries. An acoustic conservation law model describing the state of charge of a standard battery was proposed, and the change in ultrasound sound speed was related to the SOC and state of health within a battery via the density and modulus changes of the bulk battery. The time-of-flight technique was employed in the experiments.

However, so far there are no research reports with respect to VRB applications on monitoring of SOC using such a sensing approach. Since the measurement of SOC of a VRB also involves determination of concentrations, and in turn the molar fractions, of vanadium ion species existing in the electrolyte solutions, in this study we are the first to investigate the use of this novel analytical approach for effective monitoring of SOC for a VRB. In general, this study is based on the reported findings and simulation approaches as the working mechanisms, with an attempt to applying the ultrasound sensing approach to monitor the SOC of a VRB through the use of a proper empirical equation derived from the experimental data.

2. Experimental

The flow battery electrolytes are prepared in 2 M H_2SO_4 aqueous solutions, which are prepared by properly diluting concentrated sulfuric acid (Emsure® analysis grade, 95–97%) in Millipore water. A specific amount of $VOSO_4 \cdot 3.54H_2O$ compound (Alfa Aesar, 99.9%) is added to the sulfuric acid solution to prepare the V^{4+} electrolyte solution in its VO^{2+} ionic form. Then, a certain amount of the prepared V^{4+} electrolyte solution is put in 1:1 volume ratio into the positive and the negative electrode electrolyte solution storage tanks, respectively, of a flow battery test module. The test module is a flat-type, single-cell flow battery with bipolar plates made of graphite and current collector end plates made of a stainless steel material. Two pieces of carbon felts (CeTech, GF065) of 4 cm × 4 cm in geometric area and 6.5 mm in thickness are employed as electrodes, which are subjected to electrochemical oxidation pretreatment [32] and separated by a piece of Nafion® 117 membrane.

The tested battery module is first charged at constant current of 2 A until the voltage rises to 1.7 V, then it is charged at constant voltage of 1.7 V until the current drops to 0.2 A. After that, the electrolyte containing V^{5+} and V^{3+} in the positive and the negative electrode storage tanks, respectively, are taken out and stored for further use. Next, a known amount of the prepared V^{4+} electrolyte solution is put in 2:1 amount ratio into the positive and the negative electrode storage tanks, respectively, of a flow battery. Using the same preparation procedures as described above, the electrolyte solution containing V^{4+} and V^{2+} species in the positive