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Vanadium solid-salt battery: Solid state with two redox couples

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ABSTRACT

We present the "vanadium solid-salt battery" (VSSB), which has high energy density, is low cost, is easily recycled, operates at ambient temperature, and has no requirement for special solvents. The VSSB contains two types of vanadium solid salts that are supported on carbon felts with a minimal amount of hydrosulfuric acid added to moisten the ion-exchange membrane. The optimized VSSB shows a cell potential of 1.34 V, excellent reproducibility for charging and discharging for nearly 100 cycles, a high energy efficiency (87%) and a high energy density (77 W h kg^{-1} at 5 mA cm^{-2} using the carbon felt XF208). The energy density is enhanced by 250–350% compared with conventional vanadium redox-flow batteries.

1. Introduction

Recently, secondary batteries have attracted marked interest for use in electric vehicles, such as hybrid and plug-in hybrid vehicles, and "Smart Grid" electricity networks. Because these batteries need to be compact for use in vehicles or houses, the energy density, i.e., the energy stored per unit weight, must be maximized. Therefore, new batteries must be developed [1–3]. At present, lithium-ion and nickel–hydrogen batteries are widely used as power sources because of their large energy densities (approximately 100 W h kg^{-1}). However, lithium-ion batteries exhibit substantial disadvantages including (i) an uneven distribution of lithium resources in the world [4], (ii) poor environmental friendliness and safety because of the use of flammable organic electrolytes, which are potentially harmful in the case of an accident [5], and (iii) insufficient energy density for batteries in future hybrid vehicles and Smart Grid networks. Concerning inflammability, aqueous batteries such as the lead acid battery and vanadium redox-flow battery (VRFB) are advantageous; however, both possess low energy density and the former contains lead, which is toxic. The VRFB uses only vanadium [6,7], which leads to unique advantages that have been investigated in basic research [8–10] and in applications [11,12]. The fatal disadvantage of the VRFB is that the energy density is as low as 25–35 W h kg^{-1} [13], which is insufficient to meet the demands of electric vehicles and other mobile applications.

To satisfy the above-mentioned conditions (i)–(iii), we propose the new "vanadium solid-salt battery" (VSSB). The VSSB contains VOA_{2/n_A} and VA_{3/n_A} (A: counteranion with a charge of $-n_A$) in the positive and negative electrode composites, respectively, in the discharged state. Because the active materials are solid salts, the energy density is expected to be high. The energy density of the VSSB is moderate (approximately 80 W h kg^{-1}) because of the cell voltage of 1.3–1.4 V and weight of inactive components (i.e., sulfate anion and hydrated water). The use of vanadium is advantageous to the energy density because of its abundance in the earth's crust [14]; it is the 13th most abundant atom, but the eighth most abundant of the lighter elements and fourth most abundant transition element. In addition, there is an even distribution of vanadium resources in the world [4] compared with lithium. Also, by eliminating the inactive parts, the VSSB can be adapted into a vanadium solid oxide battery (VSEB) with much higher energy density.

Because the VSSB is solid, the operating conditions, especially the current density, differ from those of a liquid battery such as a VRFB [15]. Recent developments of solid materials such as carbon materials [16–21] and ion-exchange membranes [22,23] will allow further development of VSSBs. In this paper, the charging and discharging performance of a VSSB is demonstrated, where the counteranion (A) is a sulfate ion (SO_4^{2-}; $-n_A = -2$). This solid battery requires only an aliquot of acid for the membrane to function. A variety of parameters need to be characterized before evaluation of the battery performance. First, the optimal conditions for stable charging and discharging cycles (Section 3.1), membrane and electrode-active materials (Sections 3.2 and 3.3), and operation (Section 3.4) are established. Second, during investigation of

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the amount of active material and sulfuric acid required, the mechanisms behind the operation of the VSSB are discussed (Section 3.5). Finally, the theoretical limits of the VSSB are discussed with relation to the results obtained in this study.

2. Experimental

2.1. Structure of the VSSB

A schematic of a VSSB is shown in Fig. 1 and the typical specifications of the cell used in this paper are shown in Table 1. A glassy carbon disc (Tokai Carbon, Japan) of Φ 30 × t 3.0 was used as an electricity collector. The typical amount of active material mixed with carbon felt was 99.4 mg for $V(SO_4)_{1.5}{\cdot}x_3H_2O$ ($x_3 = 8.15$) and 70.8 mg for $VOSO_4{\cdot}x_4H_2O$ ($x_4 = 3.75$), where the determination of x_3 and x_4 will be described in Section 2.2. For calculation of the energy density of the battery, only the weights of the active materials were considered, because the objective was to reveal the basic performance compared with the theoretical one, and not to optimize other components such as the carbon electrodes, membranes and cell packaging. For a separator membrane in the cell, a cation-exchange membrane of Neosepta CMX C-1000 (abbreviated as “C-N”), anion-exchange membranes of Neosepta AMX A-9485 (abbreviated as “A-N”) and Selemion APS (abbreviated as “A-S”) were supplied by Asahi Glass Co., Ltd., Japan. The membranes were immersed in the 2 mol dm^{-3} H_2SO_4. They were then placed in the cell after the excess liquid was removed. Carbon felts (XF208, XF23A, XF30A, and XF30ADP14) were supplied by Toyobo Co., Ltd., Japan. The specific surface areas of the carbon felts were determined by averaging three BET (Brunauer–Emmet–Teller) adsorption measurements (one-point method) obtained using a FlowSorb III 2305 surface-area analyzer (Shimadzu Corp., Japan). Three types of cells, A, B and C, with different electrode area and/or thickness were prepared. The geometrical areas of cells A, B and C were 2.35, 2.35 and 1.17 cm^2, respectively, and the thicknesses were 3.0, 1.5 and 3.0 mm, respectively.

2.2. Preparation of the electrode composite

Oxovanadium(IV) sulfate, $VOSO_4{\cdot}x_4H_2O$, was purchased from Wako Pure Chemical Industries, Japan. A solution of $VOSO_4$ (2 mol dm^{-3}, 50 mL) in aqueous sulfuric acid (2 mol dm^{-3}) was electrochemically reduced on a mercury cathode under a constant current of 1 A using a galvanostat (HA-501, Hokuto Denko Co., Ltd., Japan). The aqueous solution was exposed to air overnight and then the excess sulfuric acid was removed by evaporation for a few days to prepare the $V(SO_4)_{1.5}{\cdot}x_3H_2O$ solid (Fig. 2). The hydration numbers of the salts were determined to be $x_3 = 8.15$, and $x_4 = 3.75$ by dissolving a known weight of each salt in water and then determining the concentration of vanadium by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The pentavalent salt $VO_2(SO_4)_{0.5}{\cdot}x_5H_2O$ and divalent salt $VSO_4{\cdot}x_2H_2O$ were prepared by electrolytic oxidation of the tetravalent salt, and electrolytic reduction from the trivalent salt, respectively (Fig. 2).

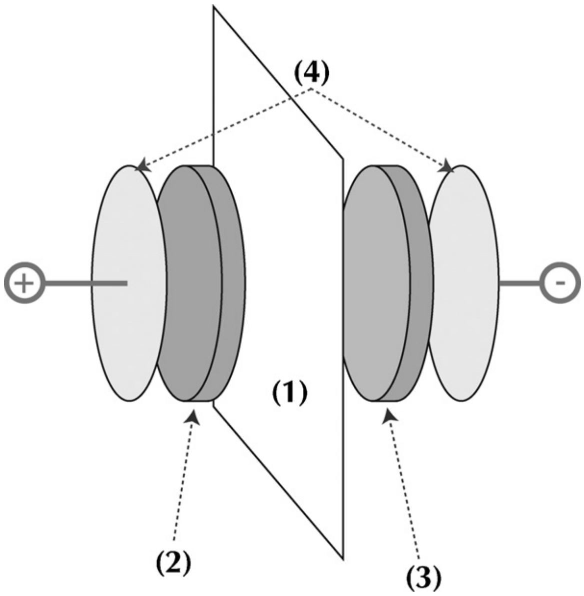

Fig. 1. Schematic of a VSSB: (1) ion exchange membrane, (2) carbon felt electrode supporting $VOSO_4{\cdot}x_4H_2O$, (3) carbon felt electrode supporting $V(SO_4)_{1.5}{\cdot}x_3H_2O$, and (4) glassy carbon electrode.

Supporting the active materials on the carbon felt was performed in two ways. One method simply involves spreading a paste of the active materials on the carbon felt (method 1, Fig. 3). Another technique involves adsorbing the active material onto the carbon felt by soaking the felt in a solution of the active material followed by vacuum drying (method 2, Fig. 3).

2.3. Measurement of charging and discharging performance

The charging and discharging performance of the cells was evaluated using a battery testing system (PFX2011, Kikusui Corp., Japan) under a constant current density of 2, 5, 10, 15, or 20 mA cm^{-2}. The terminal voltage during charging and discharging was recorded every 30 s. Charging was terminated when the terminal voltage reached to 1.80 V, and then charging was terminated at a cutoff voltage E_{CO} of 0.70, 1.0 or 1.3 V. The intermission between the discharging and discharging states and *vice versa*, known as the open circuit voltage, was recorded for 1 minute.

Table 1
Typical specifications of the optimized VSSB cell (sulfate salt system).

Category	Section where variation tested	Item	Typical setting
Performance	3.1	Cell voltage (V)	1.34
		Energy density (W h kg^{-1})	70
Membrane	3.2	Ion exchange membrane	Neosepta CMX C-1000
Electrode-active material composite	3.3	Carbon felt	XF30ADP14, 3.8 mm
		Geometric area (cm^2)	2.35
		Thickness of half cell (mm)	3.0
		Supporting method	Method 2 (See text)
	3.5	Amount of $V(SO_4)_{1.5}{\cdot}x_3H_2O$ in negative side (mol)	1.5×10^{-4}
		Amount of $VOSO_4{\cdot}x_4H_2O$ in negative side (mol)	3.0×10^{-4}
		Concentration and volume of H_2SO_4 added	2 mol dm^{-3}, 0.1 cm^3
Operation	3.4	Current density (mA cm^{-2})	5
		Cut-off voltage (E_{CO}) (V)	0.7