Electronic Supplementary Information (ESI)

Effect of phosphoric acid additive on the electrolyte of all-vanadium flow batteries

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Experiment

Preparation of the vanadium electrolyte

A tetravalent electrolyte with different concentrations of vanadium ions and sulfate ions and phosphoric acid was prepared using vanadium pentoxide as the raw material and oxalic acid as the reductant, and the redox reaction took place in a certain concentration of sulfuric acid solution. The concentrations of vanadium ions in the electrolyte were 1.0, 1.2, 1.4, 1.6, and 1.7 M, the concentrations of sulfate ions were 4.0, 4.25, and 4.5 M, and the concentrations of phosphoric acid were 0, 0.005, 0.1, and 0.15 M. Highly valent cathode electrolytes were prepared by electrolysis.

High temperature test

Take 8 ml of electrolyte in a plastic centrifuge tube, putted it in a constant temperature water bath, set the temperature at 40, 45, 50, 55 °C, respectively, and the effects of the sulfuric acid concentration, charge state, and temperature on the cathode electrolyte were tested, respectively. The condition of the electrolyte was observed every 24h and recorded.

Electrochemical tests

The trivalent and tetravalent vanadium solutions prepared as described above were used as positive and negative electrolytes for charge/discharge cycling tests, and the migration of each substance in the electrolyte was examined.

1) Assembled the electrostacks with 650 ml of electrolyte with and without 0.1 M phosphoric acid;

2) The batteries were charged to 1.55 V using 8 A constant current, then 1.55 V constant voltage charging to a current of less than 6.25 A, and discharged at a constant power of 10 W to a voltage of 1 V, with 999 cycles of charging and discharging;

3) At the completion stage of discharging in different cycles, the samples were taken to test the electrolyte valence, vanadium concentration, sulfate concentration, phosphoric acid concentration, and record the volume of electrolyte.

Table S1. Effect of phosphoric acid concentration on high temperature stability of positive electrolyte.

Phosphoric acid concentration (mol L^{-1})	SOC (%) / Temperature (℃)	Precipitate time /Days
0	85%/50	1
0.05	85%/50	3
0.1	85%/50	6
0.15	85%/50	2

Table S2. Effects of different concentrations of vanadium ions on high temperature stability of positive electrolyte.

Number of samples	Vanadium concentration (mol L^{-1})	Temperature (^{o}C)	Precipitate time (Days)
2-1	1.2	50	>30
2-2	1.4	50	17
2-3	1.6	50	6
2-4	1.7	50	2

Table S3. Influence of sulfate ion concentration, SOC, and temperature on stability of positive electrolyte.

Number of samples	Vanadium concentration (mol L^{-1})	Sulfate concentration (mol L^{-1})	SOC %	Precipitate time (Days) at different temperatures			
				40 °C	45 °C	50 °C	55 °C
3-1	1.6	4.5	85	30	30	15	5
3-2	1.6	4.5	80	30	30	20	9
3-3	1.6	4.5	70	30	30	30	30
3-4	1.6	4.5	60	30	30	30	30
3-5	1.6	4.25	85	30	30	10	3
3-6	1.6	4.25	80	30	30	17	6
3-7	1.6	4.25	70	30	30	30	21
3-8	1.6	4.25	60	30	30	30	30
3-9	1.6	4	85	30	17	6	2
3-10	1.6	4	80	30	25	12	3
3-11	1.6	4	70	30	25	25	17
3-12	1.6	4	60	30	30	30	30
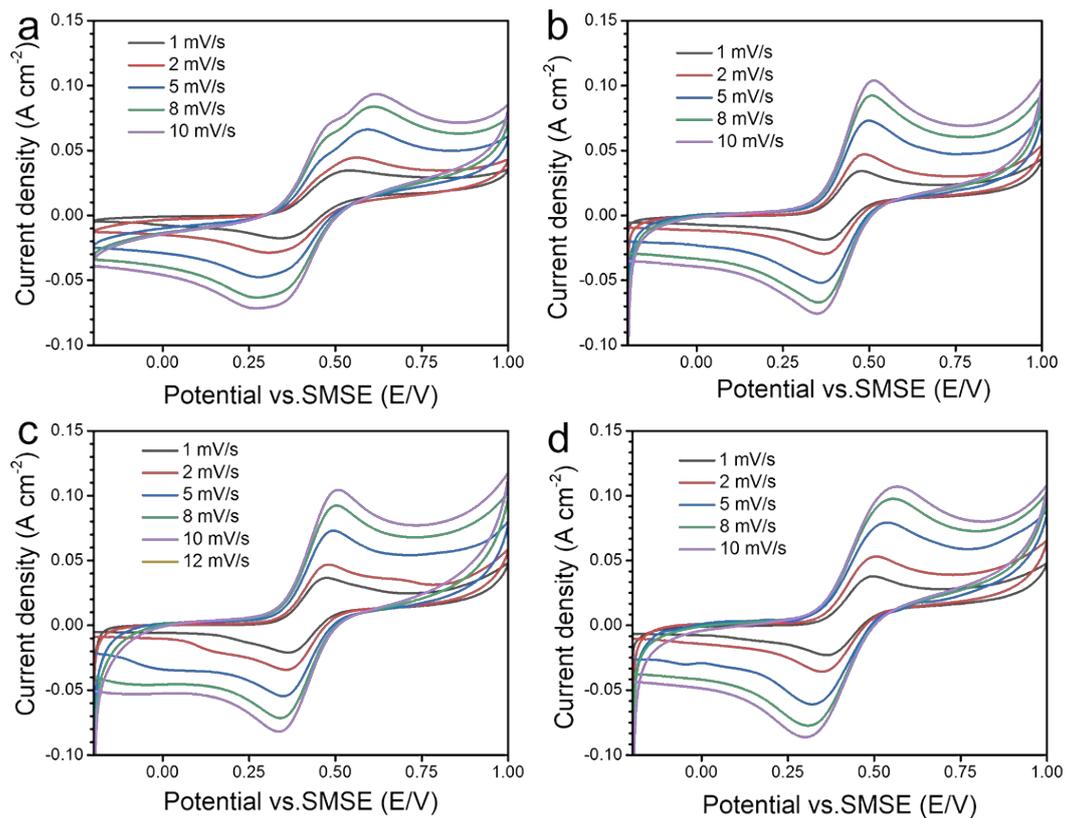
Figure S1. CV curves at different scan rates for VO^{2+}/VO_2^+ with 0.1 M $VOSO_4$ in (a) 3 M H_2SO_4, (b) 3 M H_2SO_4+50ppm Al^{3+}, (c) 0.1 M H_3PO_4 + 3 M H_2SO_4, (d) 0.1 M H_3PO_4+ 3 M H_2SO_4 +50ppm Al^{3+} solutions.
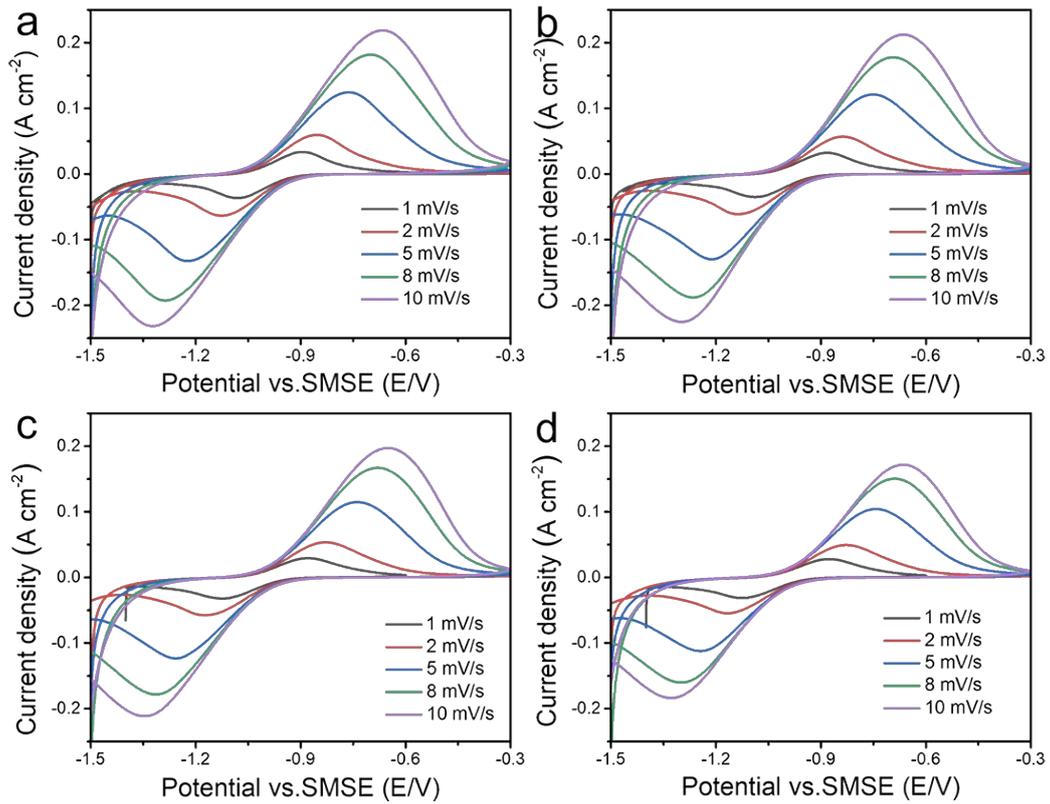
Figure S2. CV curves at different scan rates for V^{2+}/V^{3+} with 0.05 M $V_2(SO_4)_3$, in (a) 3 M H_2SO_4, (b) 3 M H_2SO_4+50ppm Al^{3+}, (c) 0.1 M H_3PO_4 and 3 M H_2SO_4, (d) 0.1 M H_3PO_4+ 3 M H_2SO_4 +50ppm Al^{3+} solutions.