Electronic Supplementary Material

Characterization and comparison of organic functional groups effects on electrolyte performance for vanadium redox flow battery

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Part 1. Viscosity and electrical conductivity measurement

The physical properties of the electrolyte in this experiment are mainly viscosity (Uzbekistan viscometer) and conductivity (Mettler-toledo S230). At 25 °C, the electrolytes of 2.0 M V(IV)/3 M H_2SO_4 with different additives content of 0 mol%, 1.0 mol%, 1.5 mol%, 2.0 mol%, 2.5 mol% and 3.0 mol%. The conductivity and viscosity affect the concentration distribution and circulation process of the electrolyte, thereby affecting the battery efficiency, capacity and loss of the battery. Table S1 and Fig. S1 show the small amount of additives slightly chang the conductivity and viscosity of all electrolytes. The electrolyte containing acetic acid has always had the lowest viscosity and the highest conductivity. It shows that acetic acid most significantly improves the viscosity and conductivity (3 mol% GAA, 259.1 ms/cm, 5.01 mm^2/s) of electrolyte. Except that the different contents of methanesulfonic acid and sulfamic acid influence the change law of viscosity and conductivity, the influence law of other additives on the electrolyte is the same.

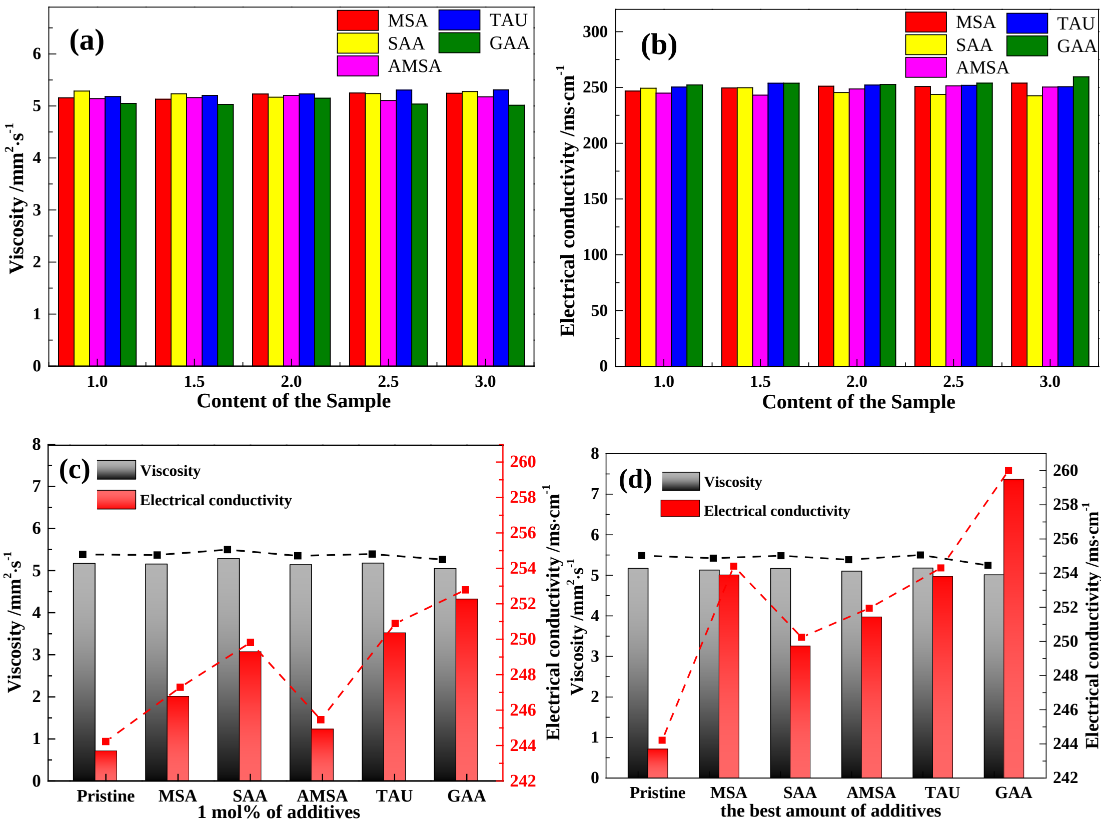

Fig. S1 Viscosity and conductivity of 2.0 M V(IV) electrolytes with different additives (a/b) the viscosity and conductivity of electrolyte with different content of additives; (c/d) the viscosity and conductivity of electrolyte with 1 mol% and the best amount of additives

In order to compare the effect of the same content of functional groups on the electrolyte. It is found from Figure S1.c that the viscosity and conductivity of the electrolyte appeared in the following descending order: SAA > TAU ≈ Pristine ≈ MSA ≈ AMSA > GAA, and GAA > TAU > SAA > MSA > AMSA > Pristine. The decrease in viscosity and the increase in conductivity may be due to the solubility of the additive itself. Additives with -SO_3H, -NH_2 and -COOH functional groups form new vanadium ions of stereoscopic structure, which enhances the vanadium interionic repulsive force, preventing the collision and aggregation of vanadium ions, making them more dispersed and faster charge transfer in solution.

Table S1 Viscosity and conductivity of electrolytes with 1 mol% different additives

Sample	Pristine	MSA	SAA	AMSA	TAU	GAA
Viscosity /$mm^2 \cdot s^{-1}$	5.17	5.16	5.28	5.14	5.18	5.05
Conductivity /$ms \cdot cm^{-1}$	243.7	246.8	249.3	244.9	250.4	252.3

Part 2. Charge-discharge measurements

The diluted positive and negative electrolytes (pristine, GAA and TAU) after cycles are UV tested in Fig. 2 The electrolytes with amino and sulfonic acid groups are without sediment, their color is blue in Fig. S2-a-I/II, indicating that the concentration of V(IV) ions is relatively high, such as the SAA, AMSA and TAU. The UV test also proves that the V(IV) peak is 765 nm, and the higher the peak intensity, the higher the ion concentration. The negative electrolytes are green, and their V(III) ions (395 nm and 578 nm) concentrations are TAU>GAA>Pristine. It can be seen that the precipitation is easier occurred of the electrolyte after charge-discharge cycles than the pure V(V) electrolyte in positive electrolyte, and the negative solution has no obvious change at room temperature.

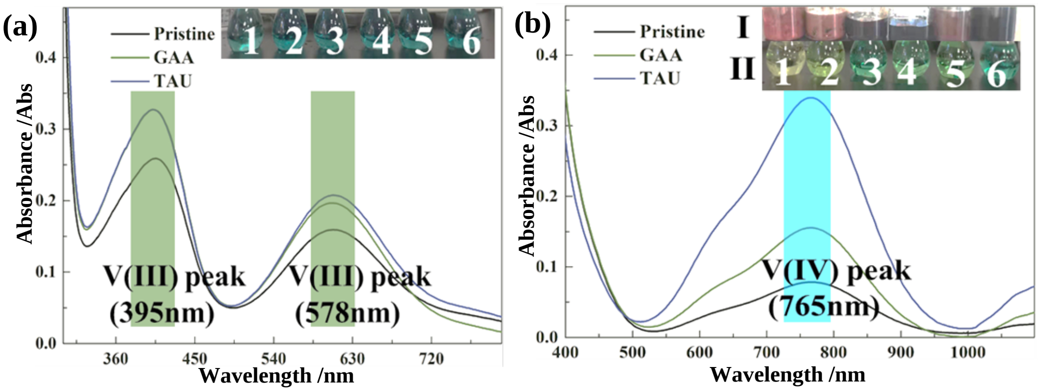

Fig. S2 (a) and (b) UV-visible analysis to test the positive and negative electrolyte after 50 cycles, where the Arabic numerals 1-6 represent respectively that Pristine, MSA, AMSA, SAA, GAA, TAU

Table S2 Battery efficiency and energy density and of the electrolyte in different cycle

Cycle	Pristine	MAS	SAA

number	C.E	E.E.	E.D.	C.E.	E.E.	E.D.	C.E.	E.E.	E.D.
1	90.9	85.5	32.5	94.9	88.9	31.2	94.6	88.9	33.8
10	91.1	86.0	27.8	95.3	89.5	31.5	95.1	89.7	35.8
20	91.6	86.3	20.3	95.1	89.7	30.4	95.2	89.7	35.5
30	91.8	86.4	13.3	95.3	89.9	28.0	95.2	89.7	33.6
40	92.1	86.1	8.4	94.5	89.4	24.9	95.1	89.8	31.4
50	91.6	85.0	5.0	95.4	90.0	21.5	95.4	90.1	29.4

Cycle	AMSA			GAA			TAU		
number	C.E.	E.E.	E.D.	C.E.	E.E.	E.D.	C.E.	E.E.	E.D.
1	94.8	89.1	32.0	95.0	89.6	35.4	94.8	88.8	31.1
10	96.5	90.7	34.1	95.7	90.3	38.5	96.3	90.2	32.9
20	95.4	89.7	34.8	95.5	90.0	36.7	96.3	90.3	34.6
30	95.3	89.7	32.1	95.8	90.1	34.2	96.4	90.4	35.2
40	95.1	89.6	28.1	95.8	90.0	32.0	96.1	90.1	34.9
50	95.0	89.3	23.5	96.1	90.5	30.6	96.3	90.6	33.9

* CE- current efficiencies; EE- energy efficiencies; ED- energy density /$Wh \cdot L^{-1}$

Part 3. Raman measurements

Table S3 The detail of assigned Raman peaks in positive electrolytes

Peak	ν/ cm^{-1}	Band assignments
1	274	ν_s $[VO(H_2O)_5]^{2+}$
2	407	ν_s $[VO(H_2O)_5]^{2+}$, ν [V=O]
3	427	δ_{as} (SO_3) $[HSO_4^-]$, ν_s (V-O-V) [V(IV)]
4	466	δ_s (O-S-O) $[V^{4+} \ldots SO_4^{2-}]$
5	488	ν_{bridge} (VO-SO) $[V^{4+} \ldots SO_4^{2-}]$
6	594	ν_s (SO_3) $[HSO_4]^-$
7	794	ν_{as} (V-O-V) [V(V)]
8	866	ν_{as} (V-O) $[VO_2^+]$, ν (VO_3^+), ν_s (V=O) $[V^{n+} \ldots SO_4^{2-}]$
9	896	ν_{as} (V-O) $[VO_2^+]$

10	986	ν_s (V-O) $[VO_2(H_2O)_4]^+$, ν_s $[SO_4^{2-}]$
11	1040	ν_s $(SO_3)[HSO_4]^-$
12	1172	ν_s (S-O) $[V^{n+} \ldots SO_4^{2-}]$,$\nu_{as}$ (S-O) $[HSO_4]^-$

* vs = very strong, s = strong, m = medium, w = weak, vw = very weak. ν = stretching, δ = bending, as = antisymmetric, s = symmetric, bridge = bridging, term = terminal.