Electronic Supplementary Information

Asymmetric vanadium flow batteries: long lifespan *via* anolyte overhang strategy

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Experimental details

The electrolyte titration and characterization details

The catholyte and anolyte were sampled at the end of the discharge process. In each step of the capacity decay curve, at least two samples were taken out to evaluate the ion concentrations of V^{2+}, V^{3+}, VO^{2+} and VO_2^+. A potentiometer (PHS-3C, Shanghai precision & scientific instrument CO., LTD) was used to conduct the potentiometric titration experiment. To prevent V^{2+} and V^{3+} from being oxidized by the oxygen in air during the test, the potentiometric titration of the anolyte was conducted under nitrogen protection. In detail, 0.10 mol L^{-1} $(NH_4)_2Fe(SO_4)_2$ (abbreviated as $Fe_{(II)}$) and 0.02 mol L^{-1} $K_2Cr_2O_7$ (abbreviated as $Cr_{(VI)}$) were prepared. The $K_2Cr_2O_7$ solution was used to define the concentration of V^{2+}, V^{3+}, VO^{2+}, and the $Fe_{(II)}$ solution was prepared to titrate the concentration of VO_2^+. Specifically, 0.2 mL of the electrolyte to be tested was removed for titration each time. Specifically, the calculate equations were showed as follows:

$$C_{II} = C_{III} = C_{IV} = (6 \times C_{Cr(VI)} \times \Delta V_{Cr(VI)}) / 0.2 = 0.6 \times \Delta V_{Cr(VI)} \tag{1}$$

$$C_V = (C_{Fe(II)} \times \Delta V_{Fe(II)}) / 0.2 = 0.5 \times \Delta V_{Fe(II)} \tag{2}$$

where C_{II}, C_{III}, C_{IV} and C_V are the concentrations of corresponding valance state of vanadium ions, the $C_{Cr(VI)}$ and $C_{Fe(II)}$ represent the ion concentrations which are in the subscripts, $\Delta V_{Cr(VI)}$ and $\Delta V_{Fe(II)}$ represent the volume changes of $K_2Cr_2O_7$ solution and Fe(II) solution before and after the potentiometric titration.

State of the half-cell	Catholyte / Cathodic reaction	External circuit	Membrane	Anolyte / Anodic reaction
Initial ionic composition	0.75 M V^{3+} + 0.75 M VO^{2+} + 2 M H^+ + 2 M HSO_4^- + 1.875 M SO_4^{2-}			0.75 M V^{3+} + 0.75 M VO^{2+} + 2 M H^+ + 2 M HSO_4^- + 1.875 M SO_4^{2-}
Pre-charge reaction	0.75 M V^{3+} + 0.75 M H_2O → 0.75 M VO^{2+} + 1.5 M H^+ + 0.75 M e^-	0.75 M e^-	0.75 M H^+	0.75 M VO^{2+} + 1.5 M H^+ + 0.75 M e^- → 0.75 M V^{3+} + 0.75 M H_2O
Ionic composition after pre-charge	1.5 M VO^{2+} + 2.75 M H^+ + 2 M HSO_4^- + 1.875 M SO_4^{2-}			1.5 M V^{3+} + 1.25 M H^+ + 2 M HSO_4^- + 1.875 M SO_4^{2-}
Charge reaction	1.5 M VO^{2+} + 1.5 M H_2O → 1.5 M VO_2^+ + 3 M H^+ + 1.5 M e^-	1.5 M e^-	1.5 M H^+	1.5 M V^{3+} + 1.5 M e^- → 1.5 M V^{2+}
Ionic composition after charge	1.5 M VO_2^+ + 4.25 M H^+ + 2 M HSO_4^- + 1.875 M SO_4^{2-}			1.5 M V^{2+} + 2.75 M H^+ + 2 M HSO_4^- + 1.875 M SO_4^{2-}
Discharge reaction	1.5 M VO_2^+ + 3 M H^+ + 1.5 M e^- → 1.5 M VO^{2+} + 1.5 M H_2O	1.5 M e^-	1.5 M H^+	1.5 M V^{2+} → 1.5 M V^{3+} + 1.5 M e^-
Ionic composition after discharge	1.5 M VO^{2+} + 2.75 M H^+ + 2 M HSO_4^- + 1.875 M SO_4^{2-}			1.5 M V^{3+} + 1.25 M H^+ + 2 M HSO_4^- + 1.875 M SO_4^{2-}

(a) Only considering the first dissociation of sulfuric acid is complete

State of the half-cell	Catholyte / Cathodic reaction	External circuit	Membrane	Anolyte / Anodic reaction
Initial ionic composition	0.75 M V^{3+} + 0.75 M VO^{2+} + 4 M H^+ + 3.875 M SO_4^{2-}			0.75 M V^{3+} + 0.75 M VO^{2+} + 4 M H^+ + 3.875 M SO_4^{2-}
Pre-charge reaction	0.75 M V^{3+} + 0.75 M H_2O → 0.75 M VO^{2+} + 1.5 M H^+ + 0.75 M e^-	0.75 M e^-	0.75 M H^+	0.75 M VO^{2+} + 1.5 M H^+ + 0.75 M e^- → 0.75 M V^{3+} + 0.75 M H_2O
Ionic composition after pre-charge	1.5 M VO^{2+} + 4.75 M H^+ + 3.875 M SO_4^{2-}			1.5 M V^{3+} + 3.25 M H^+ + 3.875 M SO_4^{2-}
Charge Reaction	1.5 M VO^{2+} + 1.5 M H_2O → 1.5 M VO_2^+ + 3 M H^+ + 1.5 M e^-	1.5 M e^-	1.5 M H^+	1.5 M V^{3+} + 1.5 M e^- → 1.5 M V^{2+}
Ionic composition after charge	1.5 M VO_2^+ + 6.25 M H^+ + 3.875 M SO_4^{2-}			1.5 M V^{2+} + 4.75 M H^+ + 3.875 M SO_4^{2-}
Discharge reaction	1.5 M VO_2^+ + 3 M H^+ + 1.5 M e^- → 1.5 M VO^{2+} + 1.5 M H_2O	1.5 M e^-	1.5 M H^+	1.5 M V^{2+} → 1.5 M V^{3+} + 1.5 M e^-
Ionic composition after discharge	1.5 M VO^{2+} + 4.75 M H^+ + 3.875 M SO_4^{2-}			1.5 M V^{3+} + 3.25 M H^+ + 3.875 M SO_4^{2-}

(b) Considering the sulfuric acid is fully ionized

Fig. S1 Reaction equations and ionic compositions of catholyte and anolyte during different status of the VFB.[1]

The detailed reactions and ionic compositions of catholyte and anolyte during different status of the VFB are illustrated in Fig. S1 (a) and (b). The sulfuric acid is a strong acid. The dissociation constants of H_2SO_4 at 25 ^oC are 1.0×10^3 (K_1) and 1.02×10^{-2} (K_2). In general, the first step of dissociation constant is larger than that of the second step. However, since the dissociation process is a dynamic equilibrium process, it's challenging to obtain the accurate value without relevant measurements.

If we assumed that only the first dissociation was complete, the simplified reactions and electrolyte compositions can be seen in Fig. S1 (a). If we assumed the sulfuric acid was fully ionized, the simplified reactions and electrolyte compositions can be seen in Fig. S1(b). It can be seen that the hydrogen ion concentrations in five types of vanadium electrolytes show the same trend in Fig. S1 (a) and (b). The

hydrogen ion concentration of VO_2^+ electrolyte ranks highest, followed by the V^{2+} electrolyte and VO^{2+} electrolyte, the $V^{3.5+}$ electrolyte and V^{3+} electrolyte in namely array. The actual value of the hydrogen ion concentration should lie between the two cases while maintain the same trend. As a result, this simplification will not affect the qualitative analysis in the following discussion. Therefore, to simplify the process, we assumed that the sulfuric acid was fully ionized and did not consider other ionic effect in this manuscript.

In an ideal case (ignoring side reactions and permeation of vanadium ions), the V^{3+} is oxidized into VO^{2+} and protons and electrons are produced at the cathode. An inverse reaction happens simultaneously at the anode in the process of pre-charge. The final consequence of this process is equivalent to that 0.75 M protons are transferred from the catholyte to anolyte, which leads to a higher proton concentration in catholyte than that in anolyte. The similar situation occurs during the charge process. When VO^{2+} ions are oxidized into VO_2^+ ions in the catholyte, an equal number of V^{3+} ions are reduced to V^{2+} ions in the anolyte, and then the reverse reactions occur in the discharge process. We find that the concentration of proton in catholyte is higher than that in anolyte at any status of the VFB (Fig. S1), leading to non-equilibrium transport of water across the membrane. Besides, the cross rates of different valence states vanadium ions (i.e., $V^{2+} > VO^{2+} > VO_2^+ > V^{3+}$)[2] and side reactions cause the non-equilibrium concentration between catholyte and anolyte. In the pre-charge process, when the vanadium ions in the catholyte is fully charged to VO^{2+}, there is not all of the vanadium ions in the anolyte converted to V^{3+}. It means that when the charge process is completed, all the vanadium ions in the catholyte are VO_2^+ while there still have some V^{3+} in the anolyte (please see detail discussion in our recent work).[3] That is, anolyte can continue to charge in theory, owing to the V^{3+} not fully changed to V^{2+}.

In summary, the non-equilibrium transport of ions (including vanadium ions), water as well as the side reactions make catholyte the limiting factor of capacity decay."

References
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2. C. Sun, J. Chen, H. Zhang, X. Han, Q. Luo, *J. Power Sources*, 2010, **195**, 890-897.
3. Y. Zhang, L. Liu, J. Xi, Z. Wu, X. Qiu, *Appl. Energy*, 2017, **204**, 373-381.
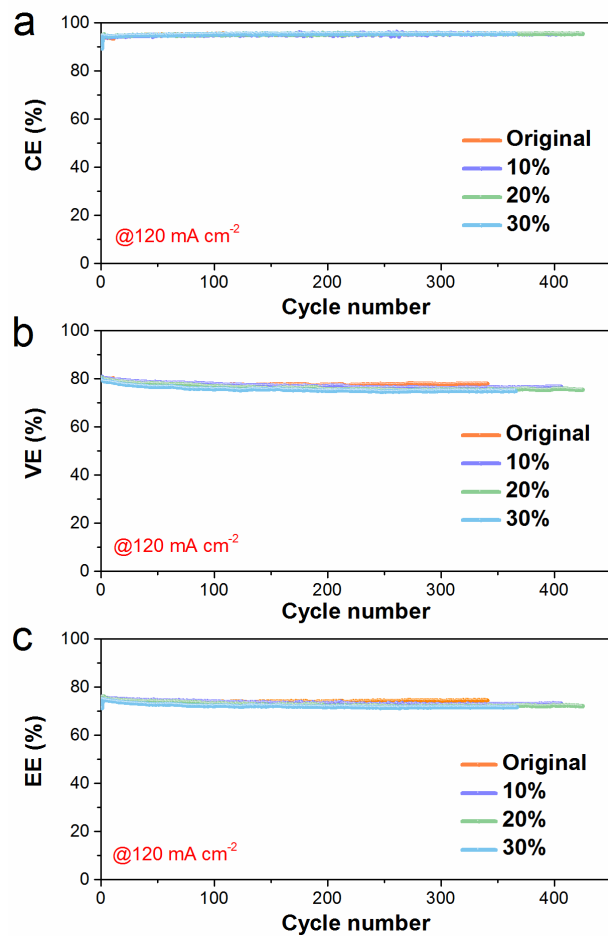
Fig. S2 The consistencies of symmetric overhang VFBs: (a) CE; (b) VE; (c) EE.
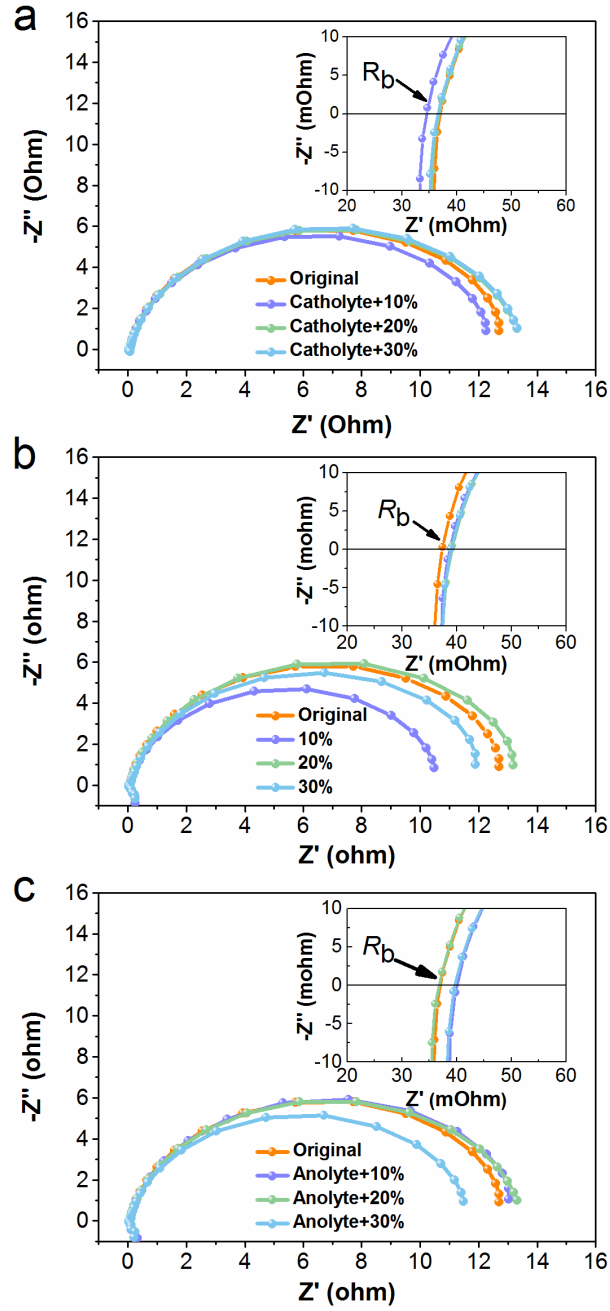
Fig. S3 Nyquist plots of all the symmetric and asymmetric VFBs: (a) catholyte overhang aVFBs; (b) symmetric overhang VFBs; (c) anolyte overhang aVFBs.

Fig. S4 Photograph of the multi-channel online monitoring system (OMS).

The cameras are connected to a computer and controlled by a specialize software to automatically record photos of the electrolyte tanks at the end of each discharge process of the batteries. Then the volume of both catholyte and anolyte can be analyzed and worked out by Matlab according to the height of electrolyte in the tanks.
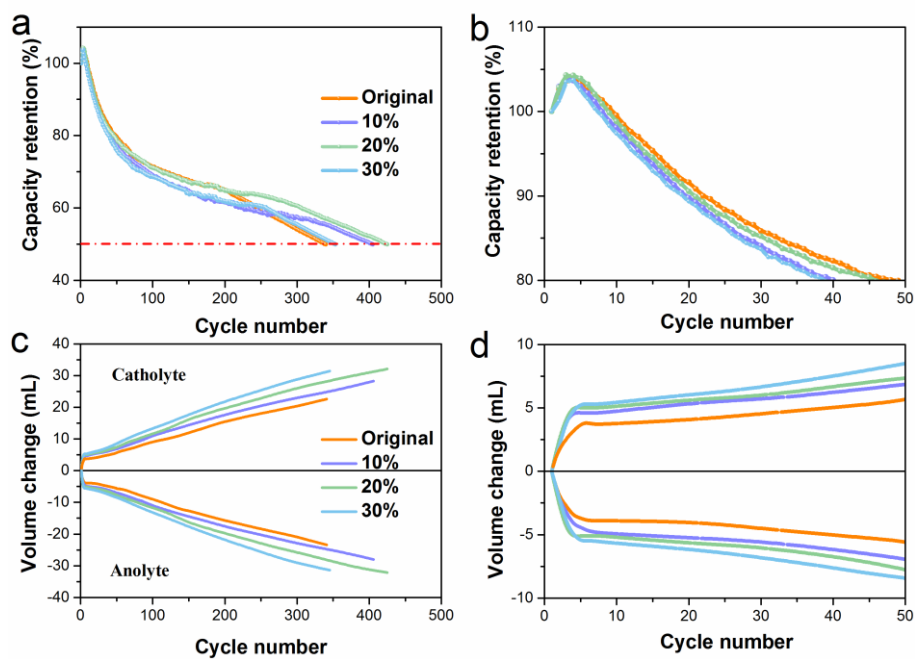
Fig. S5 Long-term cycle performance of the symmetric overhang VFBs: (a) and (b) show the capacity retention curves and their magnified figure, respectively; (c) and (d) are the regularities of volume change curves and their magnified figure, respectively.

Table S1

Cycle number and the final electrolyte composition of all the symmetric and asymmetric overhang VFBs (@50% capacity retention).

Samples	Cycle no.	V^{2+} (M)	V^{3+} (M)	VO^{2+} (M)	VO_2^+ (M)	Total vanadium (mol)	Avg. state (before)	Avg. state (after)	Δ/cycle ($\times 10^{-4}$)
Anolyte+10%	490	0.105	1.178	1.435	0.138	1.560	3.480	3.893	8.426
Anolyte+20%	484	0.075	1.231	1.415	0.149	1.640	3.450	3.851	8.281
Anolyte+30%	521	0.042	1.215	1.354	0.270	1.750	3.430	3.855	8.160
Original	341	0.067	1.238	1.418	0.110	1.490	3.500	3.814	9.218
10%	405	0.031	1.245	1.493	0.104	1.660	3.500	3.867	9.637
20%	425	0.070	1.243	1.454	0.101	1.770	3.500	3.910	9.644
30%	367	0.027	1.241	1.405	0.132	1.900	3.500	3.848	9.489
Catholyte+10%	311	0.031	1.351	1.561	0.039	1.570	3.520	3.936	13.367
Catholyte+20%	290	0.038	1.272	1.530	0.171	1.650	3.550	3.965	14.314
Catholyte+30%	287	0.050	1.245	1.581	0.192	1.740	3.570	4.003	15.071