Electronic Supplementary Information (ESI)

An Ultra-Stable Reference Electrode Development for Scaled All-Vanadium Redox Flow Batteries

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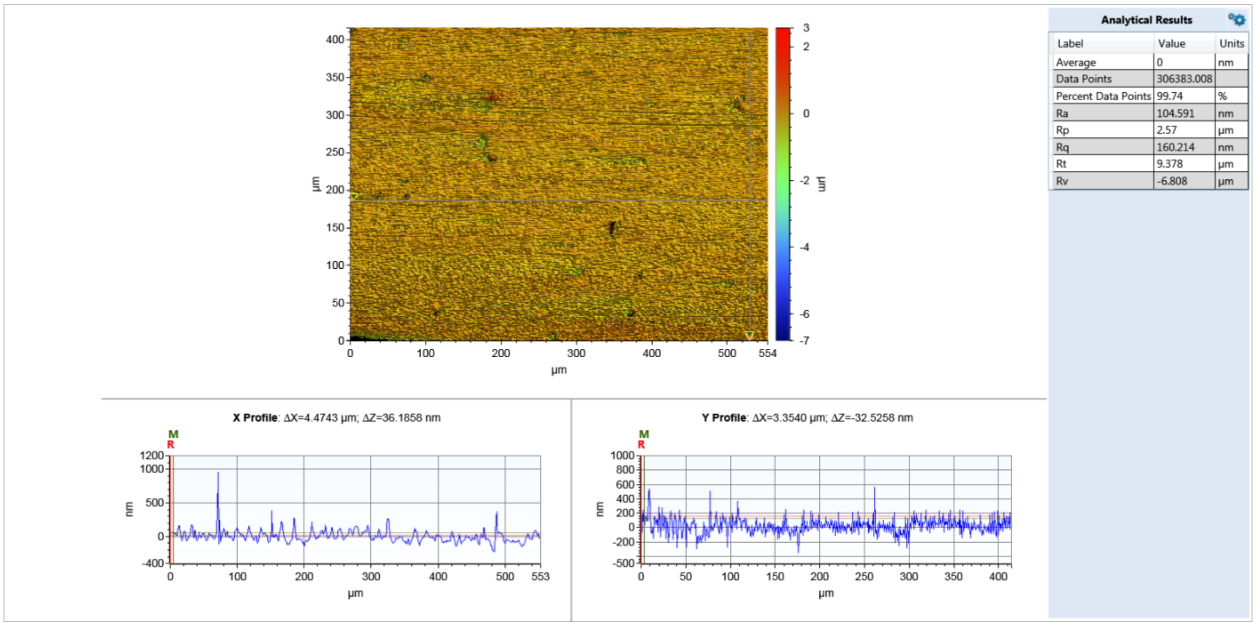
Table S1 State-of-the-art reference electrode (RE) approaches

R.E.	Type (Location)	Stability	Application	Advantage	Disadvantage
Ag/AgCl	*External	**Good**	To determine the individual overpotentials in each half-cell	Relatively stable, not influenced by the internal electrolyte environments.	▪ **Potential chloride contamination.** ▪ **A large IR drop** due to a large distance between RE and electrode.
Pt wire	**Internal	**Poor**	To decouple the cathode and anode potential or impedance	Easy to assemble	The potential of RE continued to **shift**.
Carbon cloth /fiber					
DHE (Conventional)					

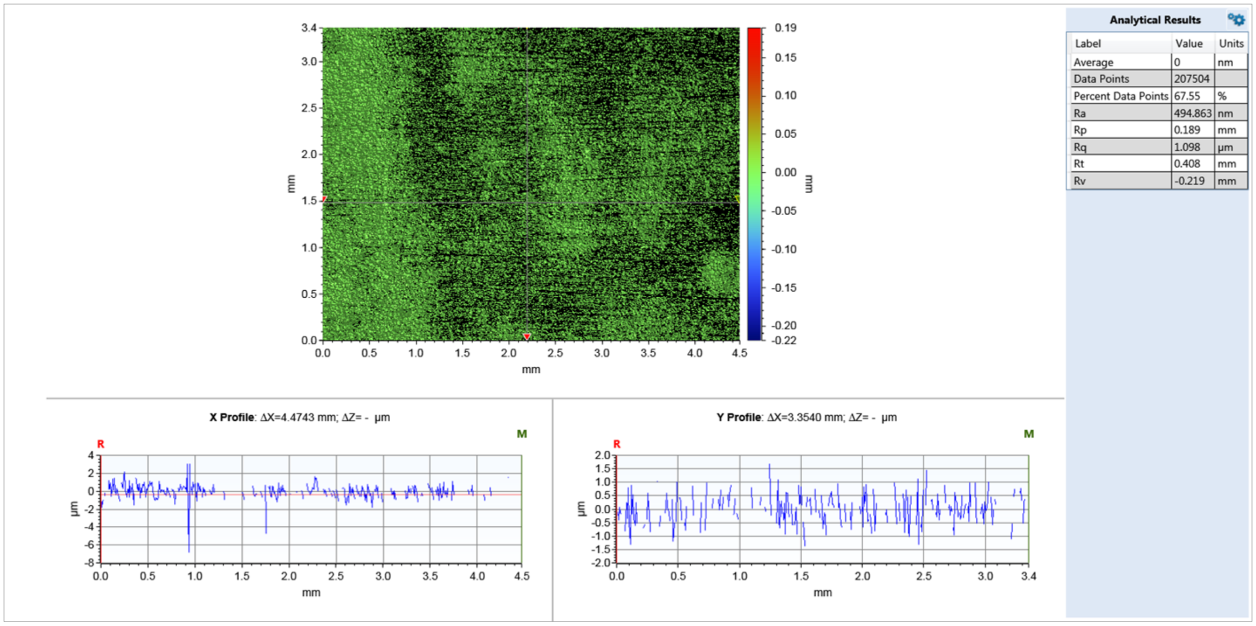
**External: inserted in the inlet or outlet tubing of the cell*

***Internal: inserted between membranes*



Analytical Results

Label	Value	Units
Average	0	nm
Data Points	306383.008	
Percent Data Points	99.74	%
Ra	104.591	nm
Rp	2.57	µm
Rq	160.214	nm
Rt	9.378	µm
Rv	-6.808	µm



Analytical Results

Label	Value	Units
Average	0	nm
Data Points	207504	
Percent Data Points	67.55	%
Ra	494.863	nm
Rp	0.189	mm
Rq	1.098	µm
Rt	0.408	mm
Rv	-0.219	mm

Figure S1 Surface roughness of the Pt foils measured by a profilometer: (a) Pt foil with smooth surface in *DHE* $_{Gen2}$, and (b) Pt foil with rough surface in *DHE* $_{Gen3}$.

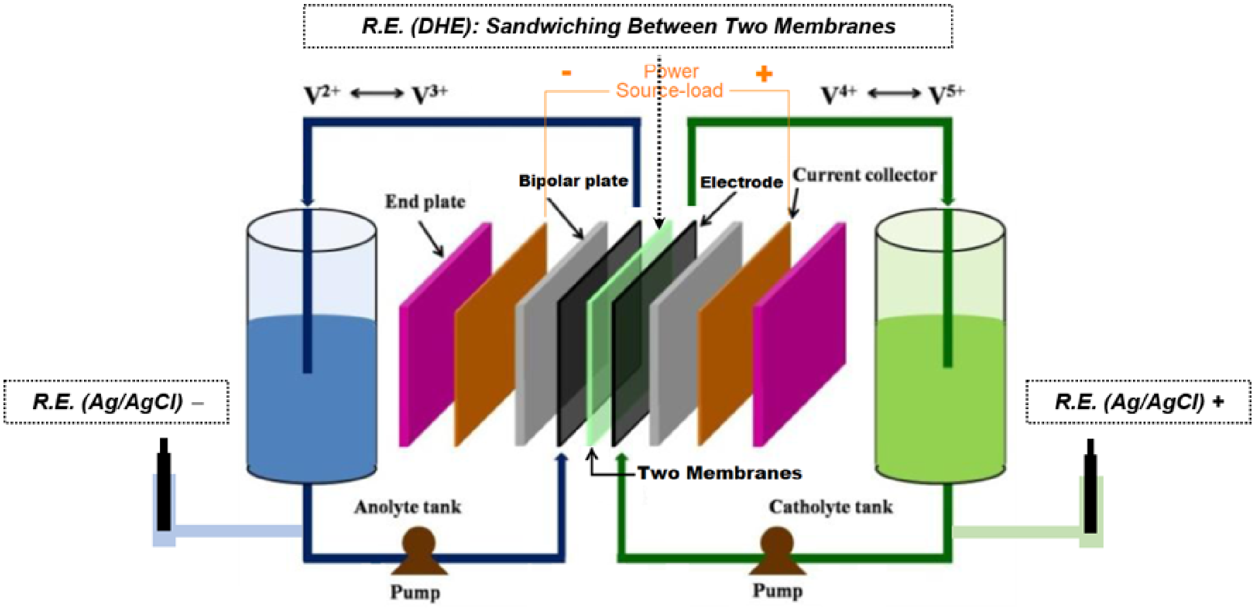
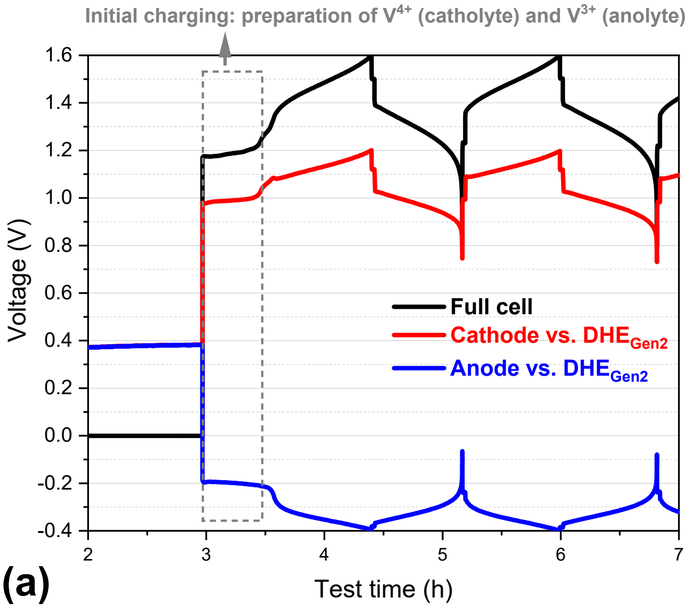
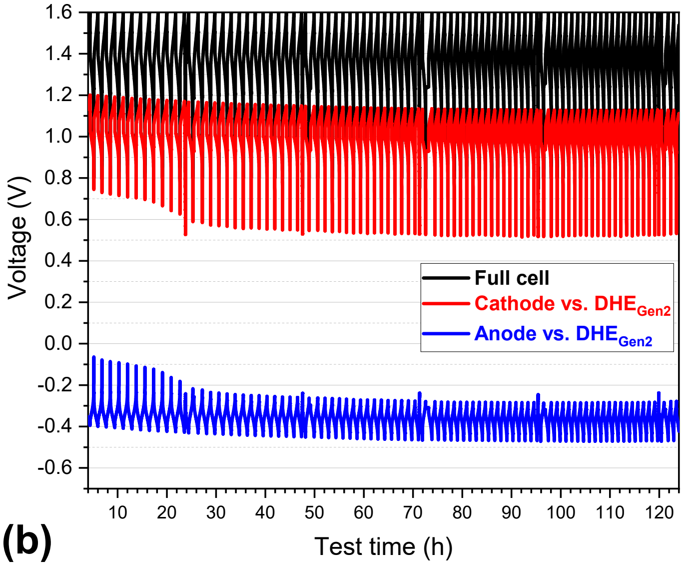


Figure S2 A scheme of an all-vanadium redox flow battery with a DHE based internal reference electrode (inserted between two membranes) and two Ag/AgCl based external reference electrodes (placed in the inlet of catholyte or anolyte respectively).


Initial charging: preparation of V^{4+} (catholyte) and V^{3+} (anolyte)
Voltage (V)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
2
3
4
5
6
7
Test time (h)
Full cell
Cathode vs. DHE_{Gen2}
Anode vs. DHE_{Gen2}
(a)


Voltage (V)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
10
20
30
40
50
60
70
80
90
100
110
120
Test time (h)
Full cell
Cathode vs. DHE_{Gen2}
Anode vs. DHE_{Gen2}
(b)

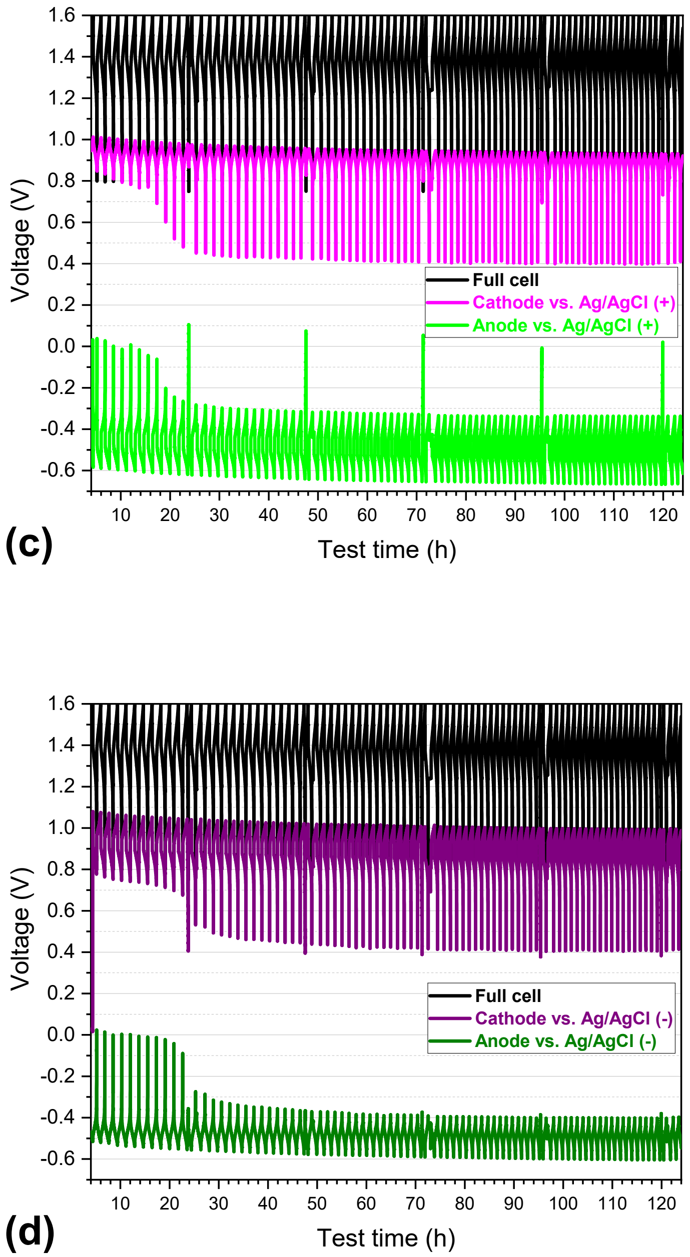


Figure S3 Voltage profiles (vs. time) with internal and external reference electrodes: individual electrode (cathode or anode) voltage vs. (a) DHE for the initial 2 cycles, (b) DHE, (c) Ag/AgCl (+) (in the catholyte inlet), and (c) Ag/AgCl (-) (in the anolyte inlet) for the initial 80 cycles.

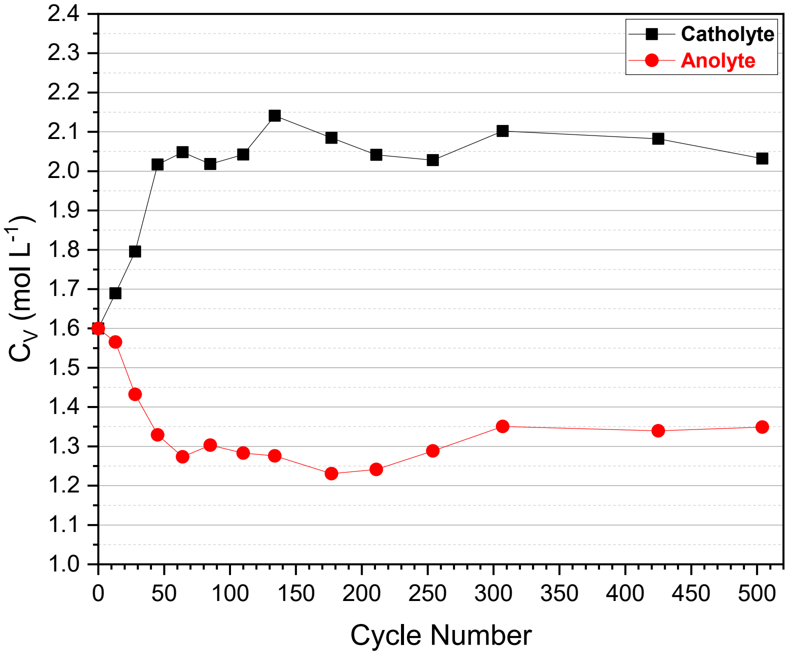


Figure S4 Total vanadium ion concentration of catholyte and anolyte as a function of cycle number, measured by inductively coupled plasma (ICP) after discharge.

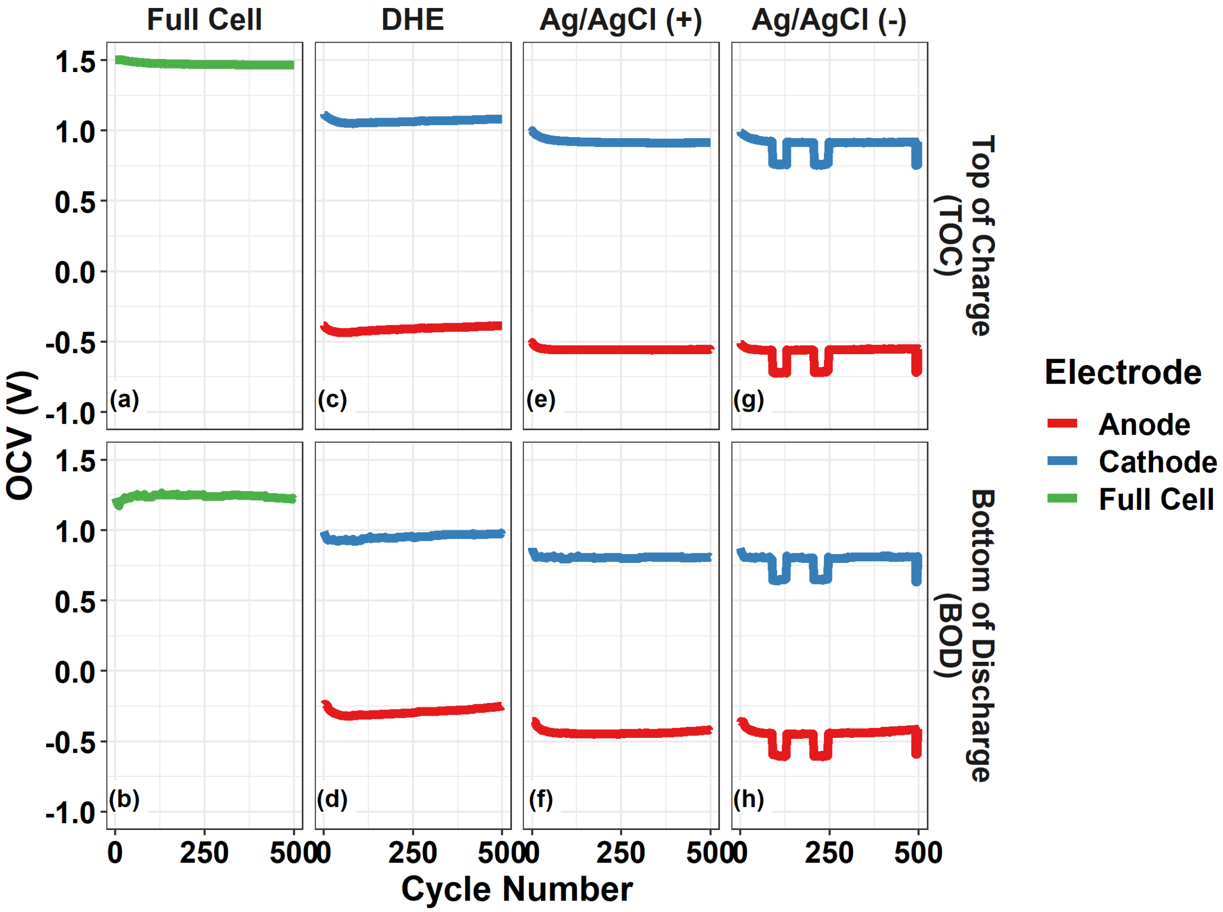
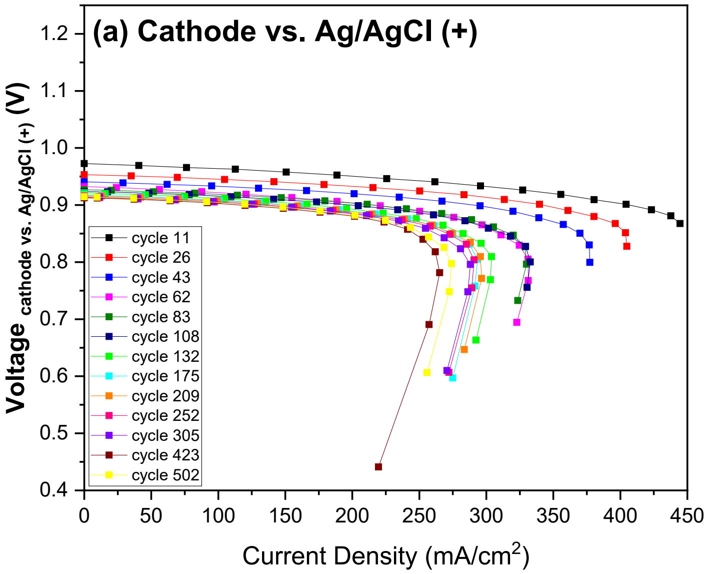


Figure S5 OCV at the top of charge (TOC) and bottom of discharge (BOD) as a function of cycle numbers for the full cell and individual electrode (cathode or anode) vs. different reference electrodes (DHE, Ag/AgCl (+) and Ag/AgCl (-)).



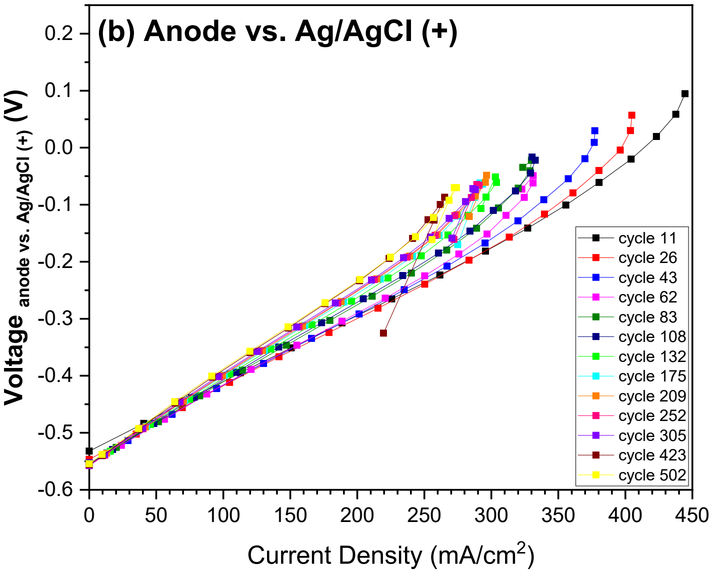


Figure S6 Polarization curves as a function of cycle numbers for (a) cathode vs. Ag/AgCl (+) and (b) anode vs. Ag/AgCl (+).