Electronic Supplementary Material (ESI) for Energy Advances.

Supporting Information

Prussian Blue Analogues with $Na_2Ni_xCo_yMn_zFe(CN)_6$-Multimetallic Structures as Positive and Hydrogen Vanadate as Negative Electrodes in Aqueous Na-Ion Batteries for Solar Energy Storage Applications

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Calculations of Diffusion Coefficient (D)

The diffusion coefficients (D) of Na ions in the host structures of PBAs are calculated from EIS data by using Eq. S1.[S1]

$D = 0.5 \times R^2 \times T^2 \times A^{-2} \times n^{-4} \times F^{-4} \times C^{-2} \times \sigma^{-2}$ ……………………………………………(S1)

Herein, R = universal gas constant

T = absolute temperature

A = geometrical area of the electrode

n = number of electron transfers per molecule during oxidation and reduction

F = Faraday constant

C = molar concentration of sodium ions (mole/cm^3)

σ = Warburg factor, which is connected to the real component of impedance (Z′)

The following equation shows the relationship between Z′ and σ.

$Z' = R_s + R_{ct} + \sigma\omega^{-1/2}$ ……………………………………………… (S2)

Wherein, ω is the frequency in EIS study.

The linear relationship profiles of Z′ with $\omega^{-1/2}$ for PBA-1, PBA-2, PBA-3 and HVO are shown in Figure S1 (a-d), respectively. The Warburg factors (σ) are calculated from the slope of the fitted straight line.

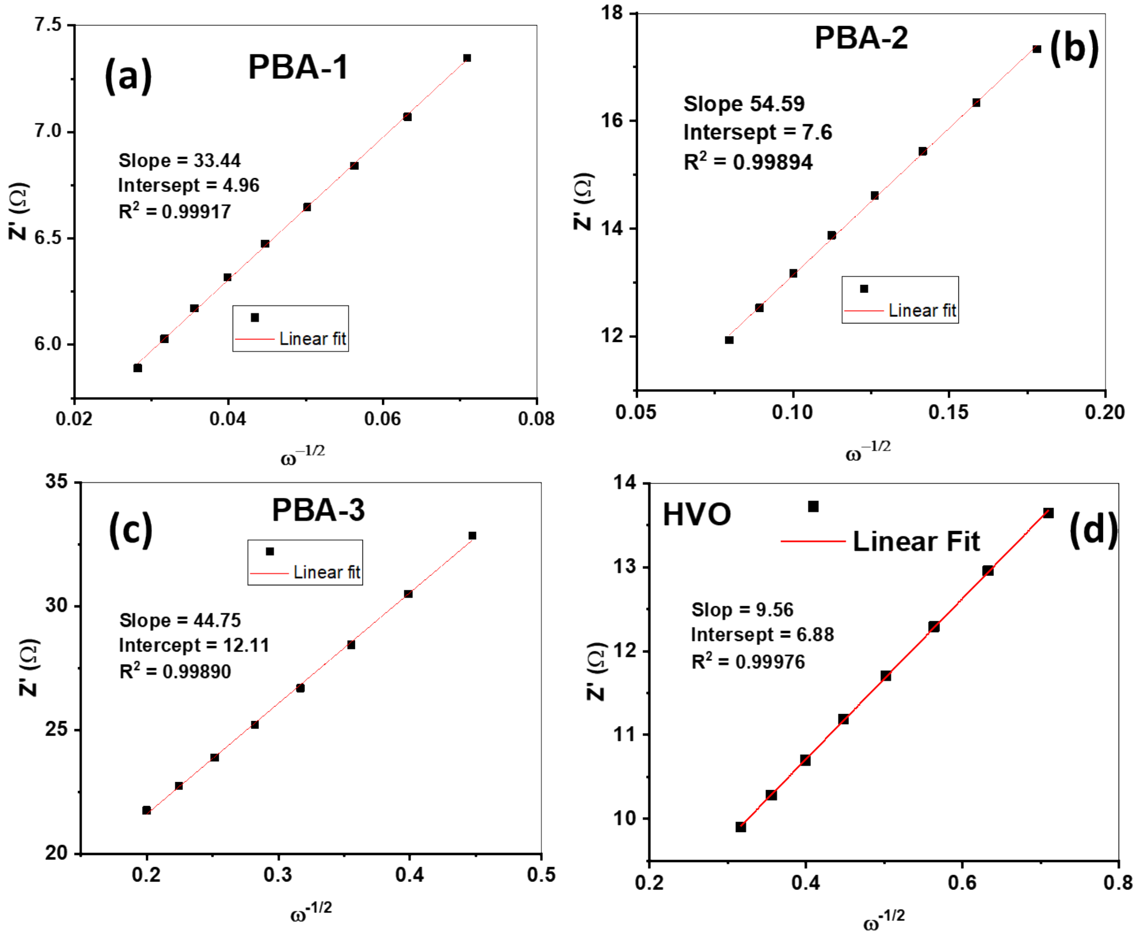

Figure S1: The linear relationship between Z′ and $\omega^{-1/2}$ at low-frequency region in EIS (ω = angular frequency) for (a) PBA-1, (b) PBA-2, (c) PBA-3 and (d) HVO.

Table S1. Calculation of Na-ion diffusion coefficient for PBA-1, PBA-2, PBA-3 and HVO

Parameter / Unit	PBA-1	PBA-2	PBA-3	HVO
R ($J\ K^{-1}\ mol^{-1}$)	8.314	8.314	8.314	8.314
T (K)	303	303	303	303
A (cm^2)	1	1	1	1
n	1.66	1.5	1.8	2
F (Coulomb mol^{-1})	96485	96485	96485	96485
#C ($mol\ cm^{-3}$)	0.0118	0.012	0.0118	0.001
σ ($Ohm\ s^{-0.5}$)	33.44	54.6	44.75	9.56
D ($cm^2\ s^{-1}$)	3.09×10^{-14}	1.68×10^{-14}	1.29×10^{-14}	2.50×10^{-11}

C value is calculated from the crystal structures of the active materials, which are established by Rietveld refinement of PXRD data.

For PBA-1 Formula unit per unit cell (Z) = 2 Unit cell volume = 558.57 Å^3 Therefore, 4 Na^+ ion present in 558.57 Å^3 Hence, 0.0118 mole Na^+ ion present in 1 cm^{-3}	**For PBA-2** Formula unit per unit cell (Z) = 2 Unit cell volume = 551.96 Å^3 Therefore, 4 Na^+ ion present in 551.96 Å^3 Hence, 0.012 mole Na^+ ion present in 1 cm^{-3}
For PBA-3 Formula unit per unit cell (Z) = 2 Unit cell volume = 558.39 Å^3 Therefore, 4 Na^+ ion present in 558.39 Å^3 Hence, 0.0118 mole Na^+ ion present in 1 cm^{-3}	**For HVO** [S2] The HVO structure does not contain Na. Hence, the concentration of Na (mol cm^{-3}) in solid structure will be same with the electrolyte's concentration. Herein, C = 0.001 mol cm^{-3}

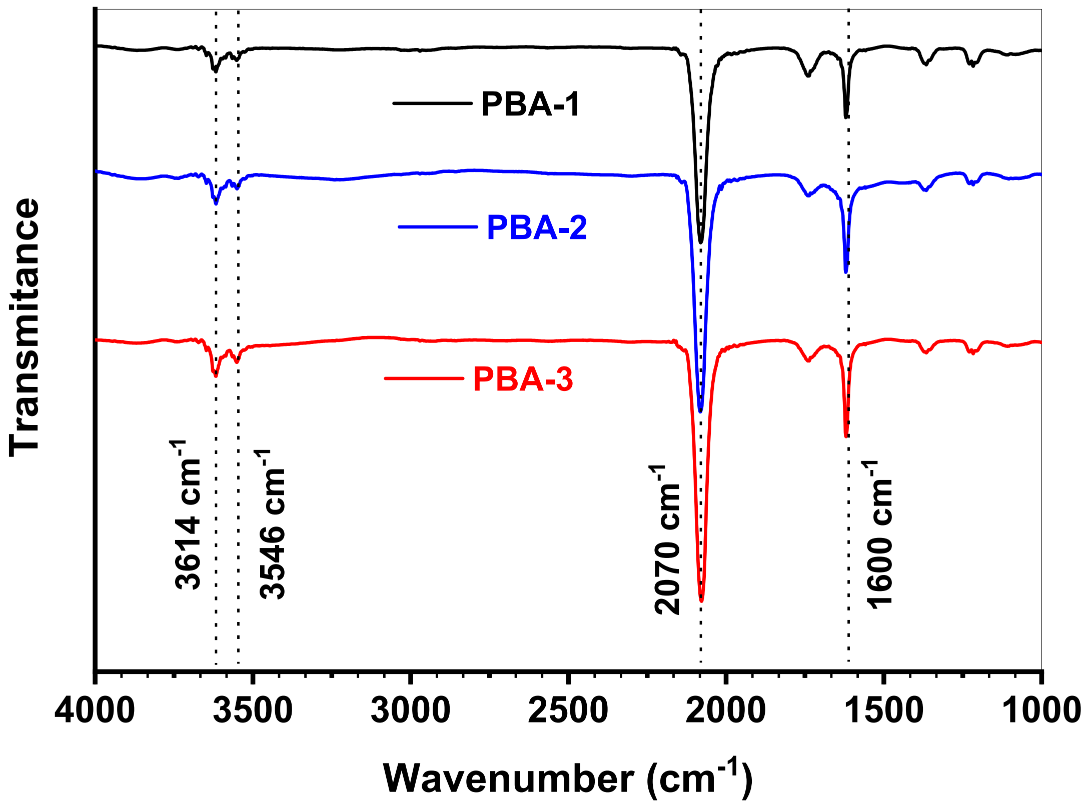

Figure S2: FT-IR spectra of PBA-1, PBA-2 and PBA-3.

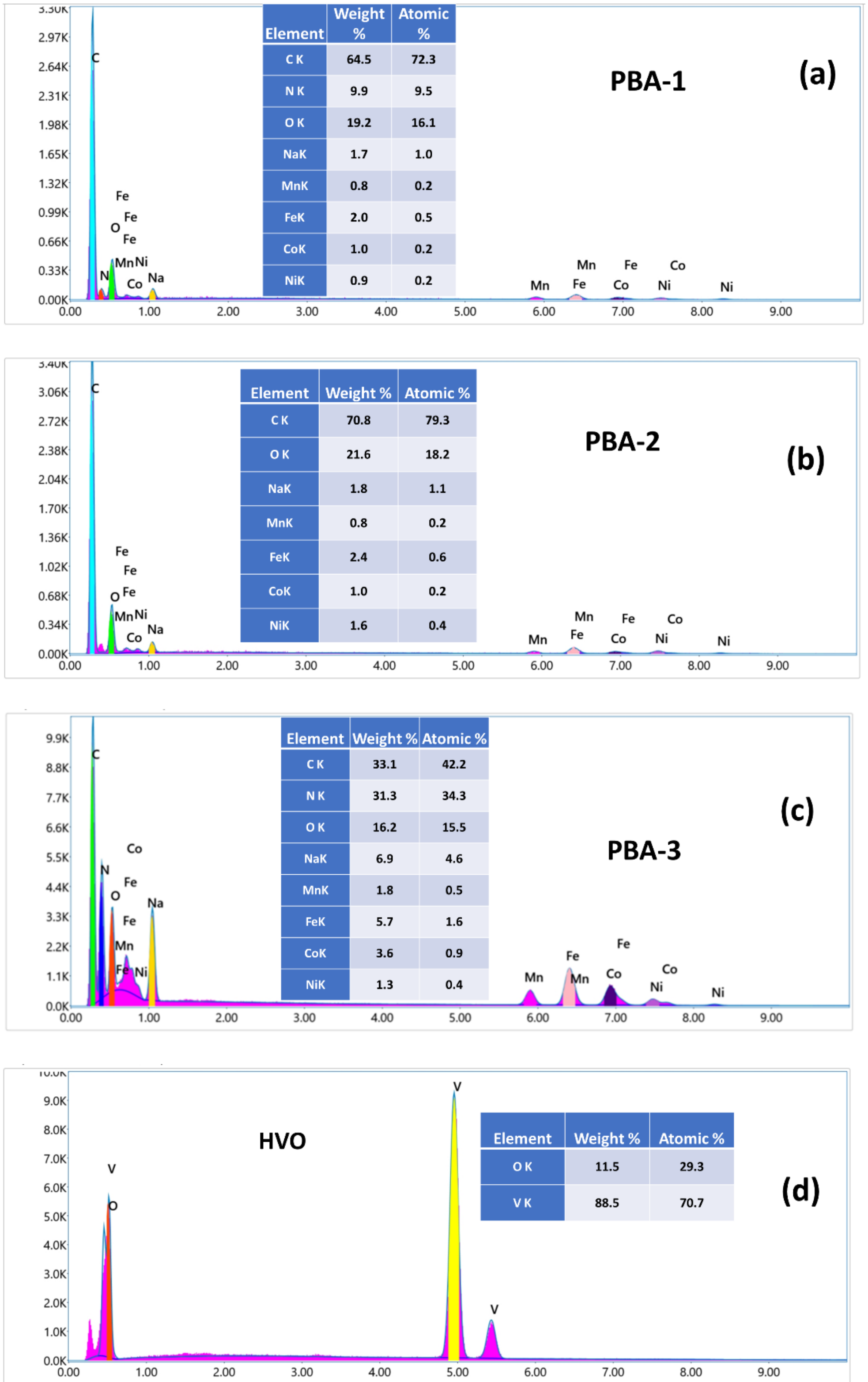

Figure S3: EDX profiles and elemental compositions of (a) PBA-1, (b) PBA-2, (c) PBA-3 and (d) HVO.

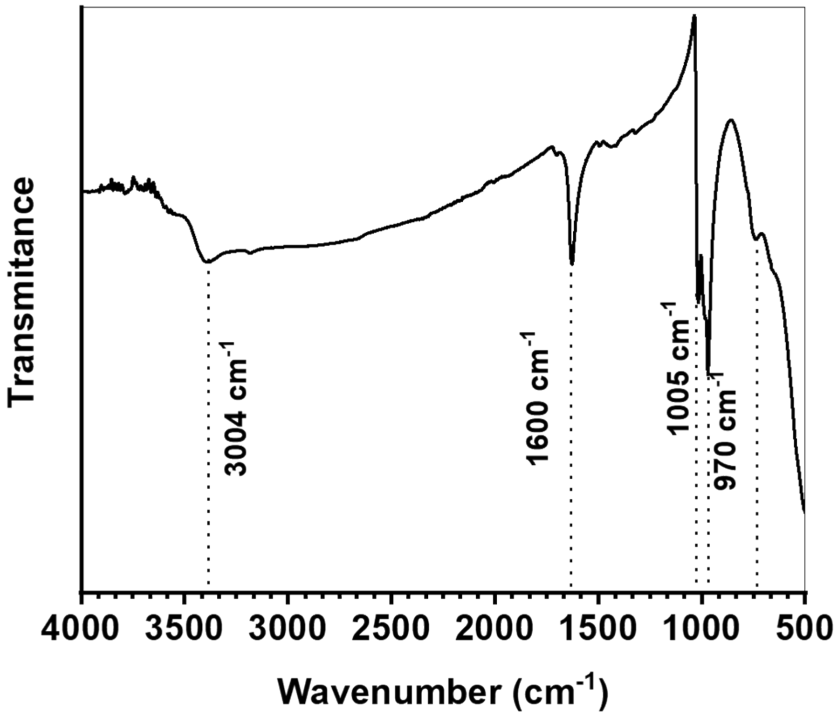

Figure S4: FT-IR spectrum of HVO.

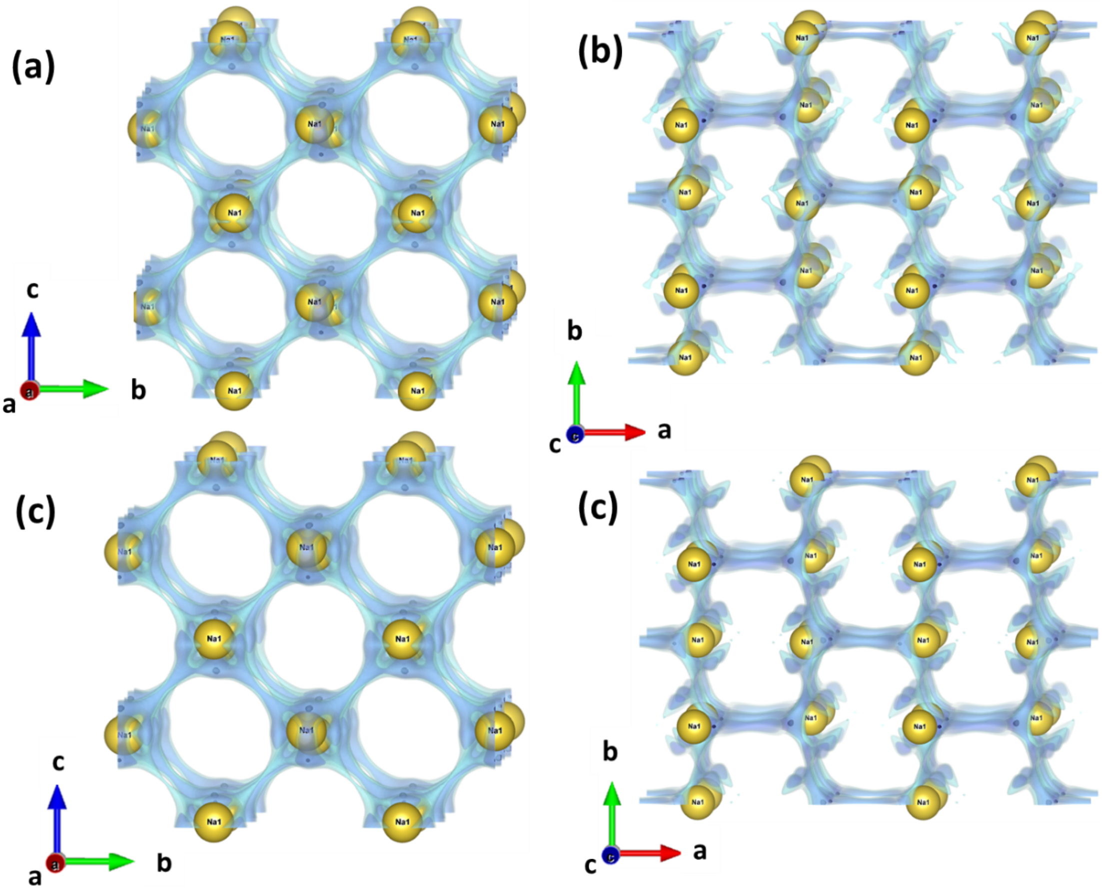

Figure S5: Na-ion diffusion pathways found from BVEL calculations for (a) PBA-2 in *b-c* plane, (b) PBA-2 in *a-b* plane, (c) PBA-3 in *b-c* plane and (d) PBA-3 in *a-b* plane.

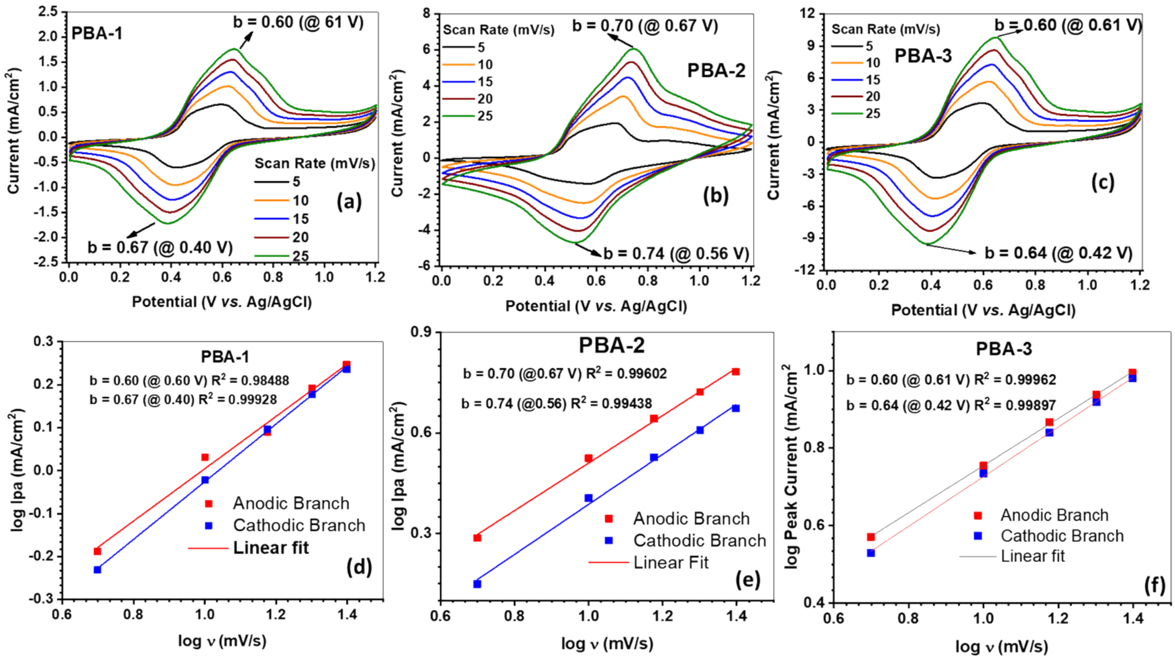

Figure S6: Cyclic voltammograms of (a) PBA-1, (b) PBA-2, (c) PBA-3 within 0-1.2 V *vs.* Ag/AgCl under the scan rate of 5 to 25 mV s^{-1}; "b" value calculations at the anodic/cathodic peaks for (d) PBA-1, (e) PBA-2, (f) PBA-3.

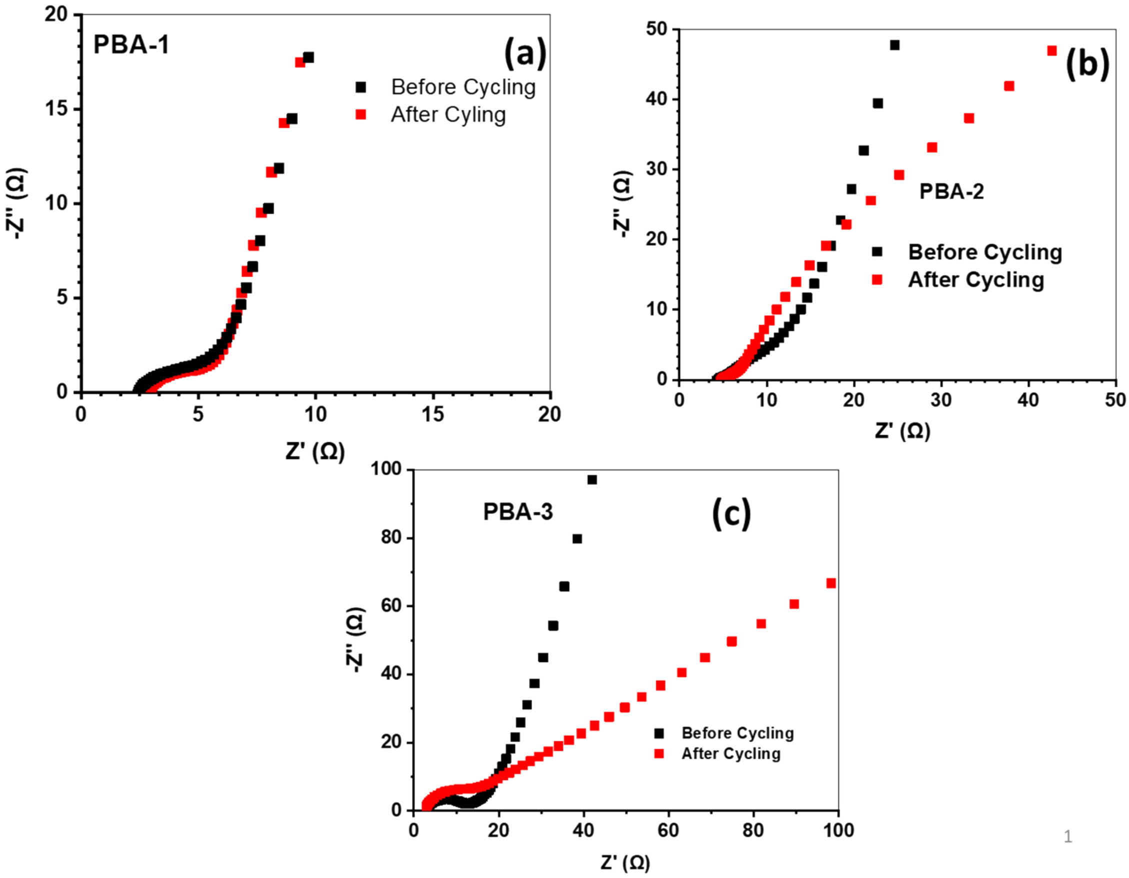

Figure S7: Nyquist plots at before and after cycling experiments for (a) PBA-1, (b) PBA-2 and (c) PBA-3.

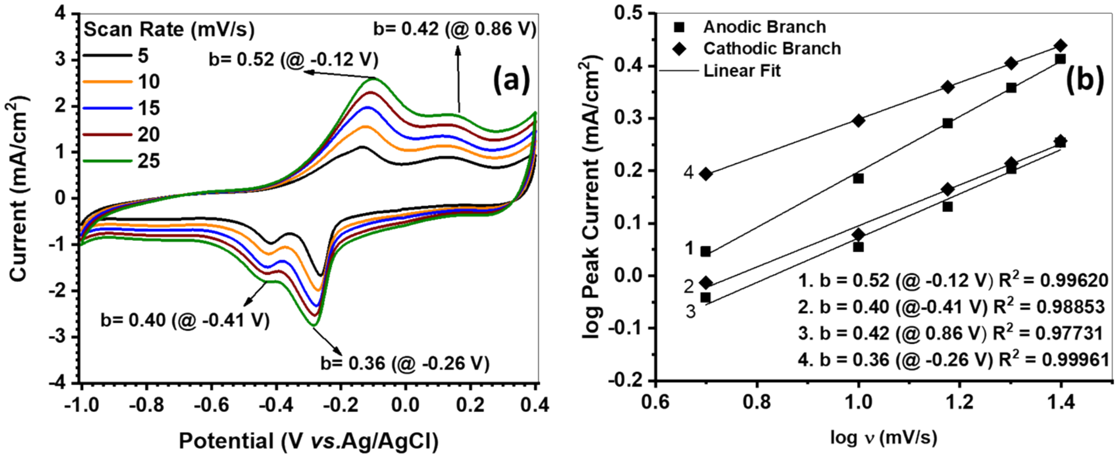

Figure S8: (a) Cyclic voltammograms of HVO within 0.4 to -1.0 V *vs.* Ag/AgCl under the scan rate of 5 to 25 mV s^{-1}; (b) "b" value calculations at the cathodic/anodic peaks for HVO.

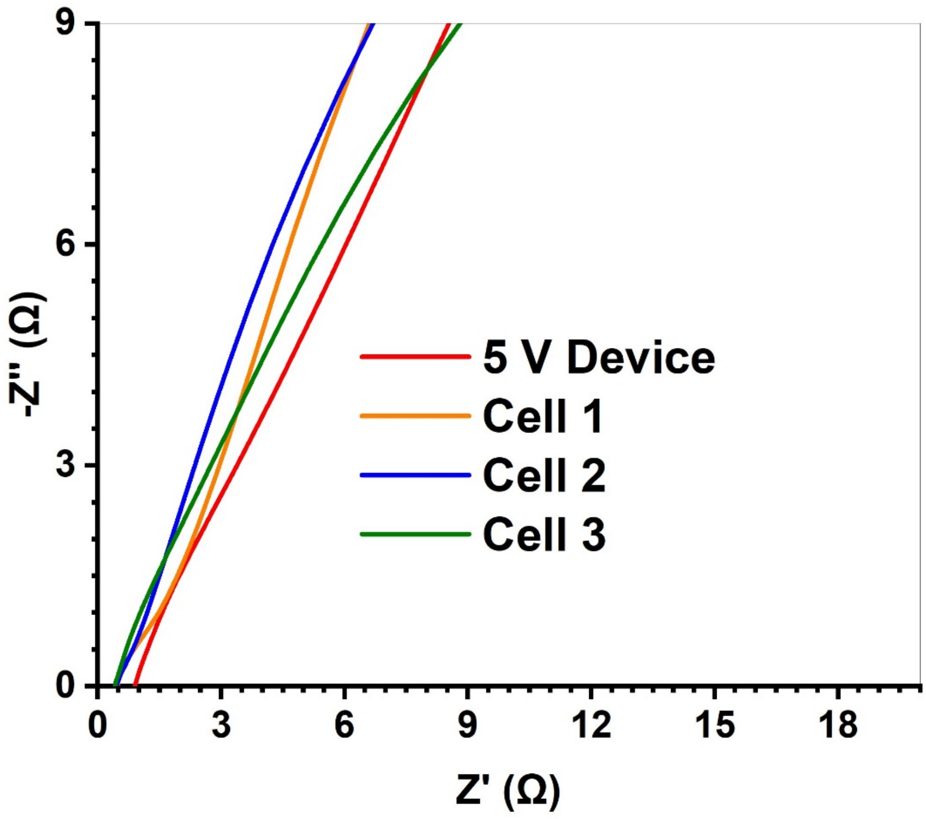

Figure S9: Nyquist plots for 5V device along with three constituent cells at their discharged states.

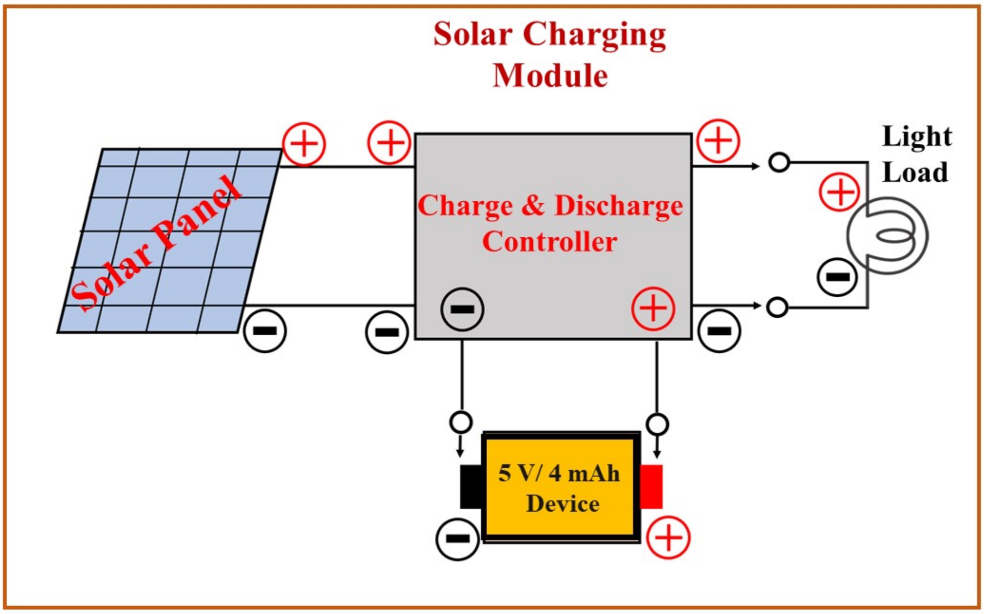

Figure S10: Schematic representation of customs-built solar-charging cum LED-discharging module for prototype battery testing.

References

S1. Y. Zhang, Z. Su and J. Ding, Synthesis and electrochemical properties of Ge-doped $Li_3V_2(PO_4)_3/C$ cathode materials for lithium-ion batteries. *J. Alloys Compd.*, 2017, **702**, 427-431.

S2. C. Liu, Z. Neale, J. Zheng, X. Jia, J. Huang, M. Yan, M. Tian, M. Wang, J. Yang and G. Cao, Expanded hydrated vanadate for high-performance aqueous zinc-ion batteries. *Energy & Environmental Science,* 2019, **12**, 2273-2285.