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[Supporting Information]

Silver Vanadium Bronze, β-$Ag_{0.33}V_2O_5$: Crystal-Water-Free High-Capacity Cathode Material for Rechargeable Ca-ion Batteries

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1. Supporting Figures

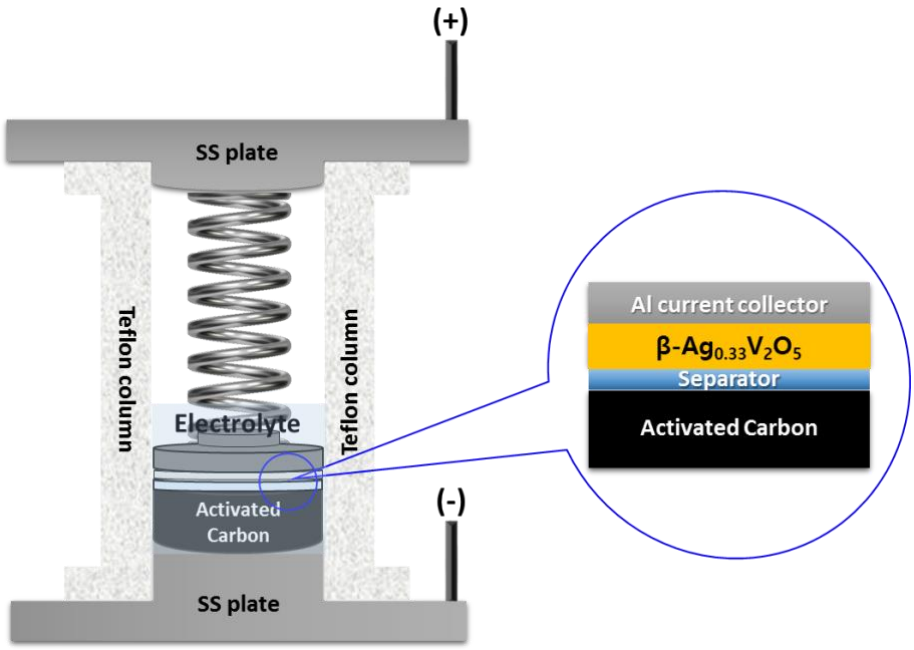

Fig. S1. Schematic illustration of the homemade cell.

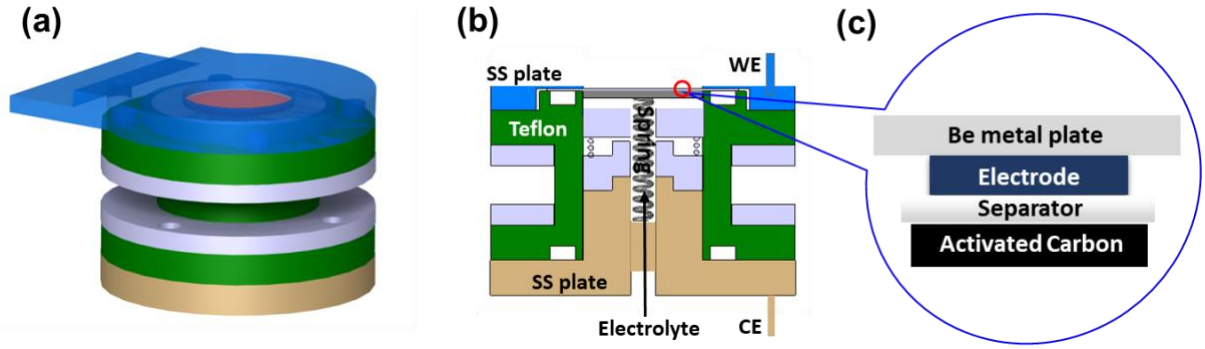

Fig. S2. Schematic configurations for in-situ XRD cell.

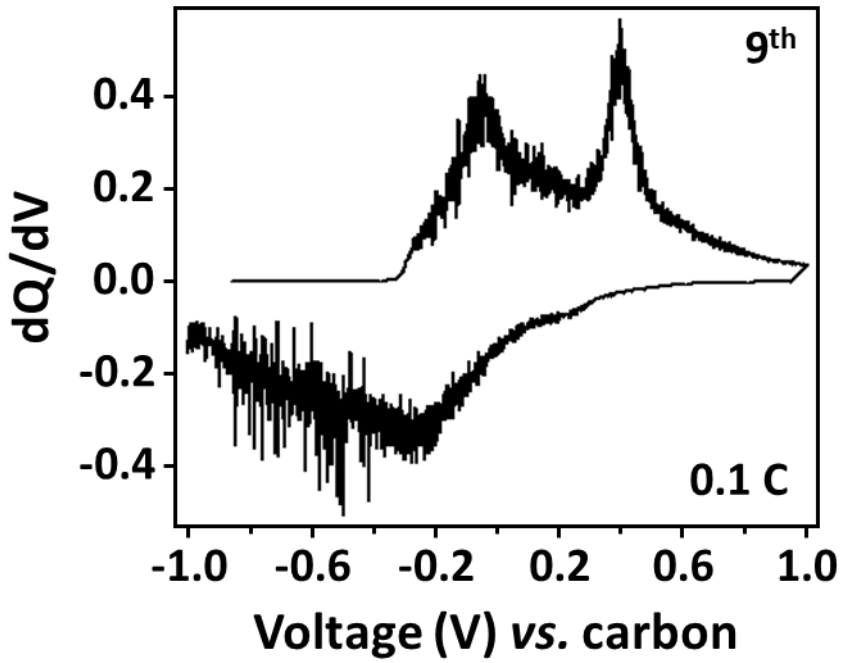

Fig. S3. dQ/dV plot for ninth galvanostatic cycle in Figure 2b.

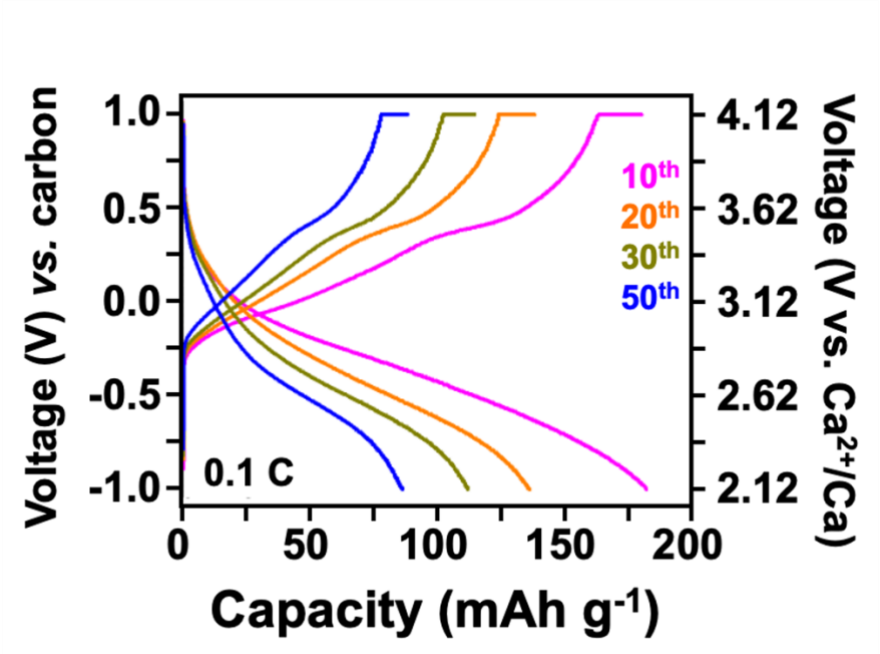

Fig. S4. Galvanostatic discharge–charge cycles of β-$Ag_{0.33}V_2O_5$ after the activation cycles at 0.1 C rate and 30 °C in 0.5 M $Ca(BF_4)_2$ in EC/PC (1:1 v/v)

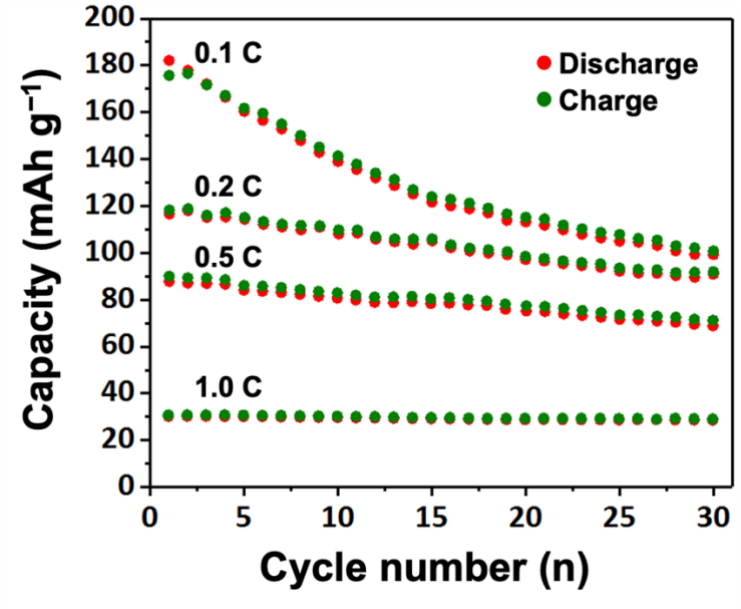

Fig. S5. Rate performance of β-$Ag_{0.33}V_2O_5$ at 0.1, 0.2, 0.5, and 1 C rates in 0.5 M $Ca(BF_4)_2$ in EC/PC (1:1 v/v) at 30 °C. These data were obtained after the electrochemical activation process for eight cycles at 0.1 C rate.

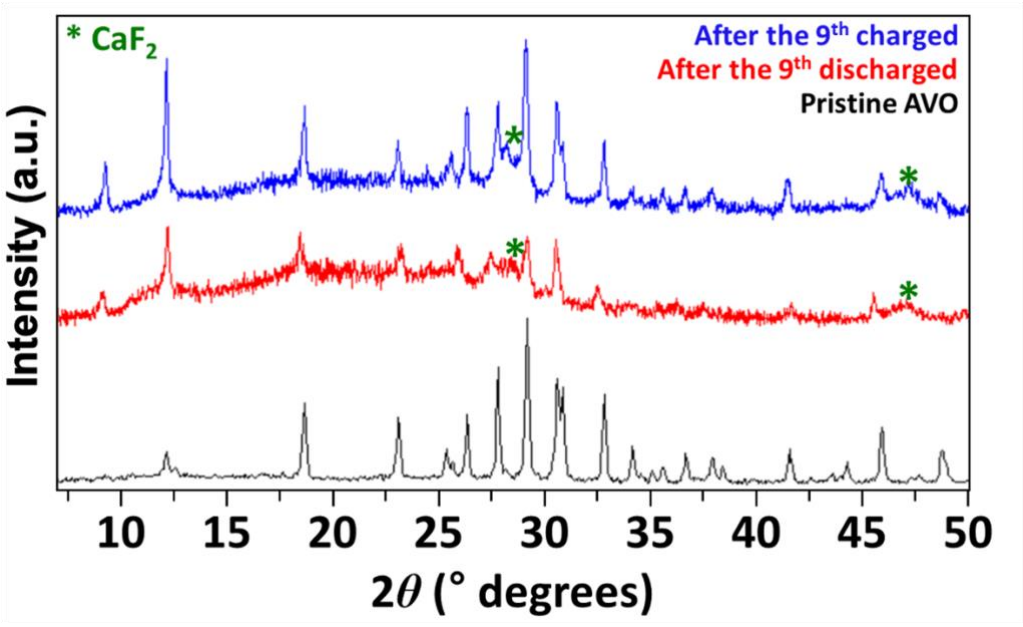

Fig. S6. Ex-situ XRD patterns of β-$Ag_{0.33}V_2O_5$. Pristine (black), ninth discharged (red), ninth charged (blue), and CaF_2 (denoted by green stars).

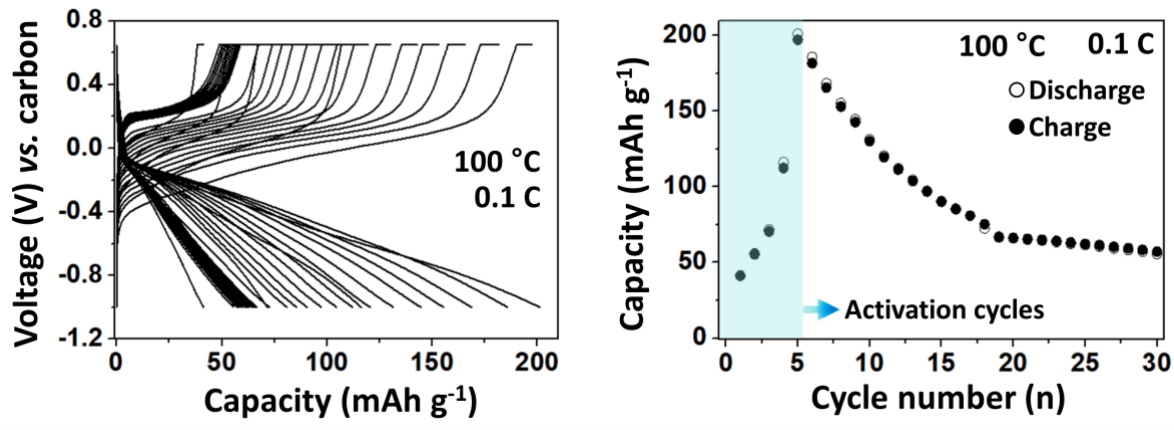

Fig. S7. Electrochemical properties of β-$Ag_{0.33}V_2O_5$ at 100 °C in 0.5 M $Ca(ClO_4)_2$ in EC/PC (1:1 v/v) at 0.1 C rate. (a) Galvanostatic discharge–charge cycles and (b) cyclability and Coulombic efficiency for 30 cycles.

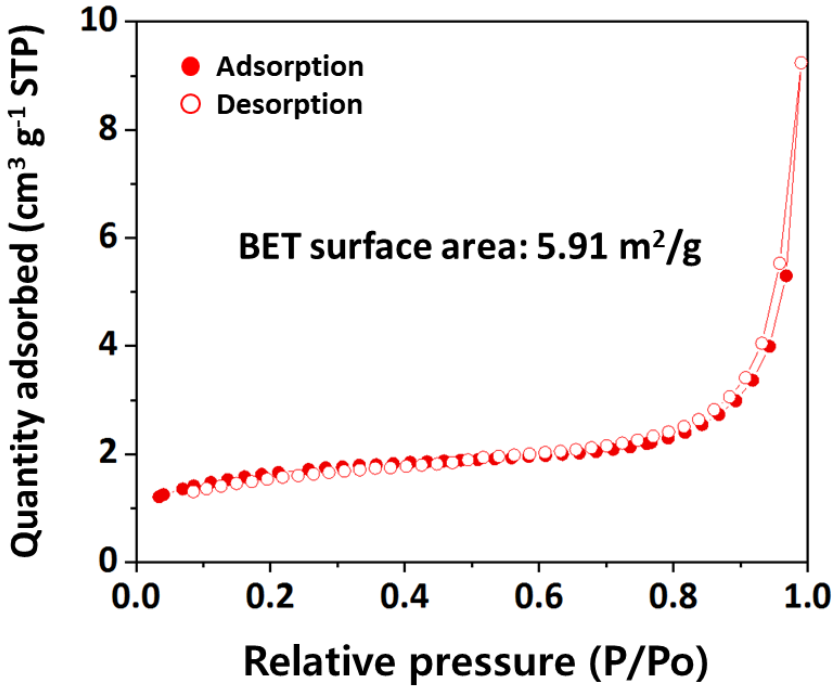

Fig. S8. Nitrogen sorption isotherm for β-$Ag_{0.33}V_2O_5$ (●, adsorption; ○, desorption).

2. Supporting Tables

Table S1. Crystallographic data and powder X-ray Rietveld refinement results for β-$Ag_{0.33}V_2O_5$: atomic coordinates, site occupancies, isotropic displacement parameters, and reliability factors at room temperature.

Crystal System	Monoclinic
Space Group	*C 2/m* (no. 12)
Lattice Parameter, Volume, Z	a = 15.373(1) Å, b = 3.6112(2), c = 10.064(1) Å β = 109.68(1)° V = 526.10(6) Å^3 *Z* = 6

Atoms	x	y	Z	Wyckoff	Occupancy	$U_{iso} \times 10^2$
Ag1	0.9961	0.0	0.5965	4i	0.5	1.25
V1	0.1167	0.0	0.119	4i	1.0	1.25
V2	0.3379	0.0	0.1008	4i	1.0	1.25
V3	0.2880	0.0	0.4102	4i	1.0	1.25
O1	0.0	0.0	0.0	2a	1.0	1.25
O2	0.1075	0.0	0.2729	4i	1.0	1.25
O3	0.1332	0.5	0.0776	4i	1.0	1.25
O4	0.2634	0.0	0.2232	4i	1.0	1.25
O5	0.4369	0.0	0.2187	4i	1.0	1.25
O6	0.3143	0.5	0.0539	4i	1.0	1.25
O7	0.3986	0.0	0.4731	4i	1.0	1.25
O8	0.2420	0.0	0.5733	4i	1.0	1.25

* R_p = 0.123, R_{wp} = 0.165, R_{exp} = 0.140, $R(F^2)$ = 0.115, χ^2 = 1.391

Table S2. Selected interatomic distances (Å) for structure of β-$Ag_{0.33}V_2O_5$

Ag-Ag	1.986 (1) Å	Ag-O2	2.382 (1) Å
Ag-O5	2.548 (1) Å	Ag-O7	2.408 (1) Å
Ag-O7	2.671 (1) Å	V1-O1	1.790 (1) Å
V1-O2	1.602 (1) Å	V1-O3	1.890 (1) Å
V1-O4	2.143 (1) Å	V1-O6	2.323 (1) Å
V2-O3	1.989 (1) Å	V2-O4	1.944 (1) Å
V2-O5	1.583 (1) Å	V2-O6	1.878 (1) Å
V2-O6	2.333 (1) Å	V3-O4	1.790 (1) Å
V3-O7	1.602 (1) Å	V3-O8	1.994 (1) Å
V3-O8	1.885 (1) Å		

Table S3. Elemental ratios estimated from ICP analysis for β-$Ag_{0.33}V_2O_5$ (AVO) electrodes.

	ppm			Relative atomic ratio		
	Ca	**Ag**	**V**	**Ca**	**Ag**	**V**
Pristine AVO	N.D.	66.01	191.1	N.D.	0.33	2.00
0.5M $Ca(BF_4)_2$ in PC:EC						
After the 1st discharged	-	13.40	42.19	-	0.30	2.00
After the 1st charged	-	12.81	39.32	-	0.31	2.00
After the 9th discharged	-	4.83	33.84	-	0.13	2.00
After the 9th charged	-	2.87	37.02	-	0.07	2.00
0.5M $Ca(ClO_4)_2$ in PC:EC						
After the 5th discharged	10.44	3.514	31.99	0.83	0.10	2.00
After the 5th charged	0.432	1.735	34.16	0.03	0.05	2.00

N.D.: not detected