

# Support Information

## Electrode Reaction Mechanism of $\text{Ag}_2\text{VO}_2\text{PO}_4$ Cathode

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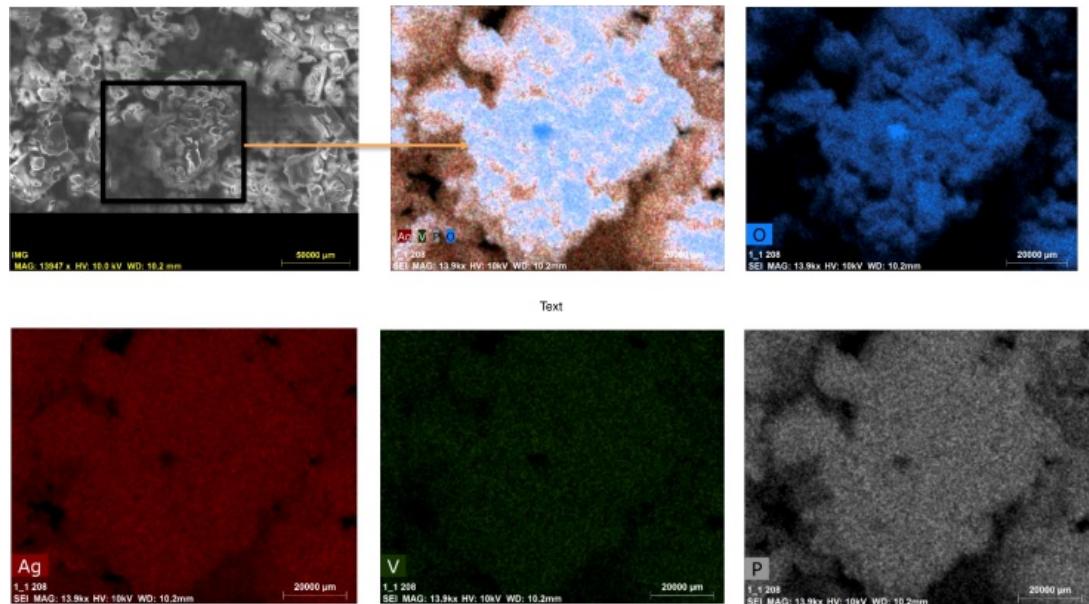
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*Key words:* Cathode, Li-ion battery,  $\text{Ag}_2\text{VO}_2\text{PO}_4$ , *in-situ*, pair-distribution function, XPS, XAS, molecular dynamics

Table S1. SEM-EDS results of as-made  $\text{Ag}_2\text{VO}_2\text{PO}_4$ .

Elements	Atomic %	Cal. Atomic %
Oxygen	54.72	60
Silver	19.33	20
Vanadium	13.71	10
Phosphorus	10.58	10
Carbon	1.67	

(a)



(b)

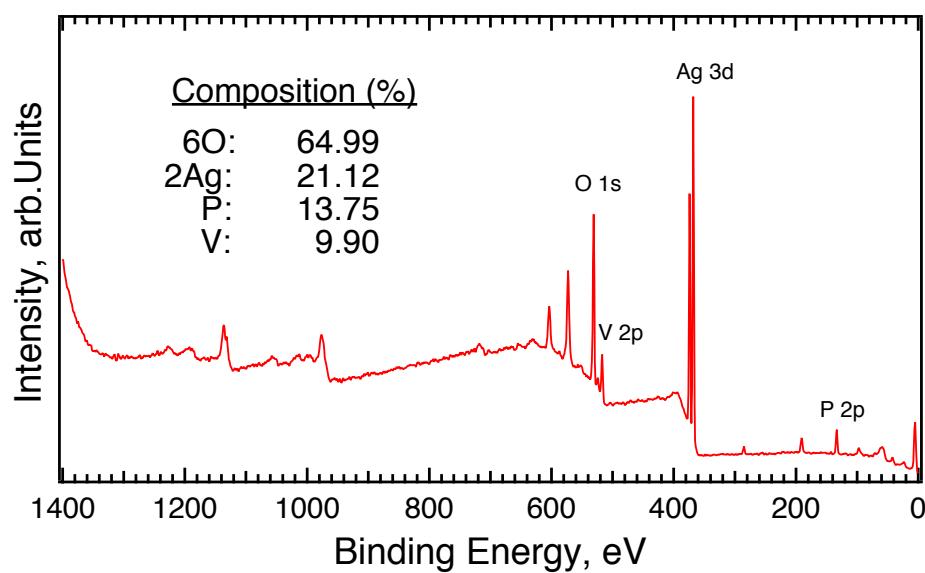


Figure S1. (a) SEM images and EDS mapping of as-made  $\text{Ag}_2\text{VO}_2\text{PO}_4$ ; (b) surface composition of  $\text{Ag}_2\text{VO}_2\text{PO}_4$  shown by XPS.

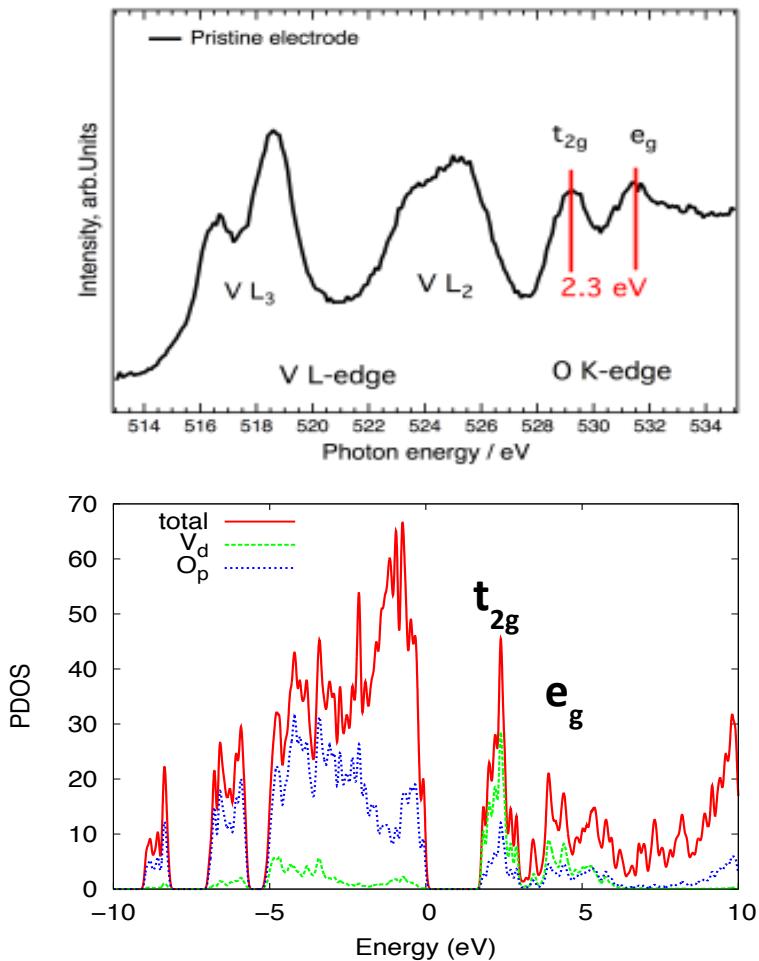


Figure S2. (Top) The V L-edge and O K-edge XAS of  $\text{Ag}_2\text{VO}_2\text{PO}_4$  powder, which displays a  $\text{V}^{5+}$  line-shape and 2.3 eV splitting between the unoccupied  $e_g$  and  $t_{2g}$  states (highlighted). (Bottom) The GGA (P)DOS of  $\text{Ag}_2\text{VO}_2\text{PO}_4$ , a 2.3 eV energy separation is observed between the  $e_g$  and  $t_{2g}$  states (highlighted).

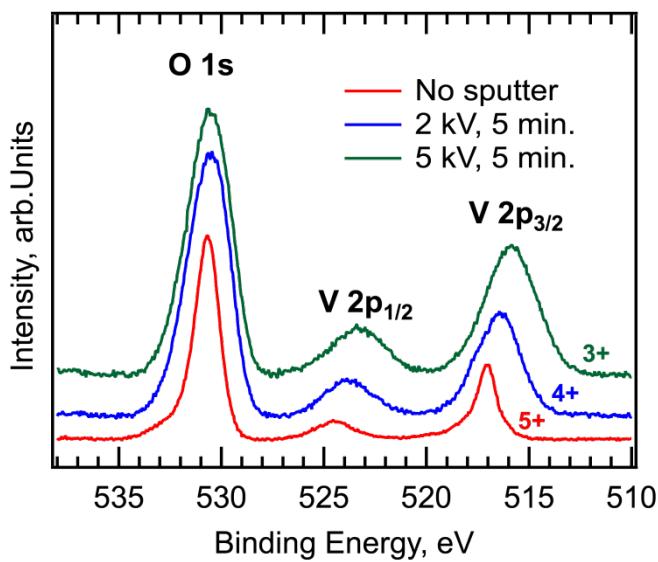


Figure S3. Sputtering effect on XPS O1s and V2p region of  $\text{Ag}_2\text{VO}_2\text{PO}_4$ . The binding energy shift in the V 2p<sub>3/2</sub> peak is consistent with the  $\text{V}^{5+}$ ,  $\text{V}^{4+}$  and  $\text{V}^{3+}$  oxidation assignments. The O:V peak area variation reflects compositional changes associated with the preferential sputtering.

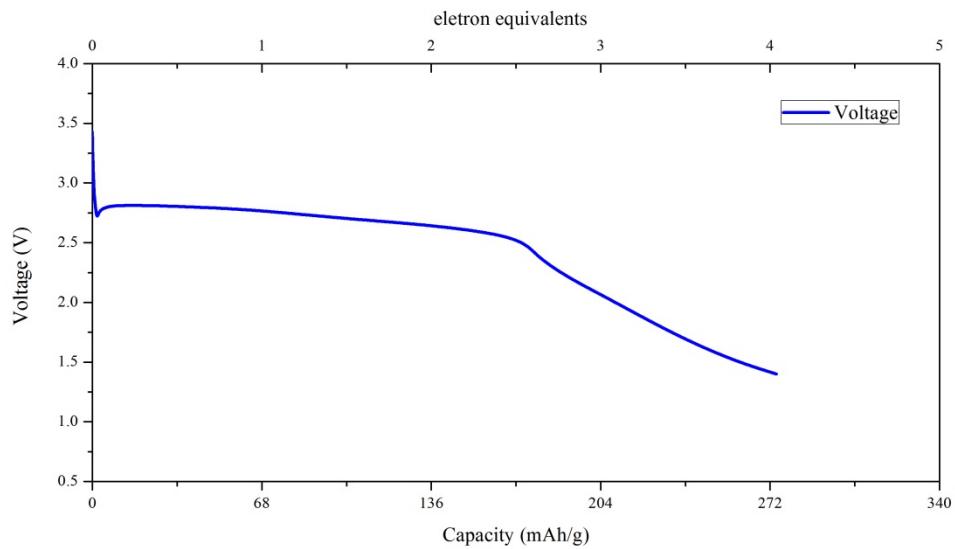


Figure S4. Electrochemistry of in-situ PDF experiment of  $\text{Ag}_2\text{VO}_2\text{PO}_4$ .

Table S2. Atomic pairs of Ag-O, Ag-Ag, V-V, V-P, Ag-V, and Ag-P in  $\text{Ag}_2\text{VO}_2\text{PO}_4$  structure within the range of 2.8-4.0 Å.

Atomic Pairs	Distances (Å)
Ag-O	2.862
Ag-Ag	3.03
Ag-O	3.082
V-V	3.106
V-P	3.202
V-P	3.237
Ag-Ag	3.268
Ag-Ag	3.319
Ag-P	3.361
Ag-V	3.371
Ag-O	3.426
V-O	3.555
Ag-P	3.578
V-O	3.582
Ag-Ag	3.592
V-O	3.61
Ag-P	3.679
Ag-V	3.729
Ag-O	3.73
Ag-O	3.733
Ag-O	3.753
V-O	3.759
Ag-O	3.795
Ag-V	3.845
Ag-O	3.894
Ag-O	3.984
Ag-P	3.989