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Electronic Supplementary Information (ESI): $Li/Ag_2VO_2PO_4$ Batteries: The Roles of Composite Electrode Constituents on Electrochemistry

David C. Bock[a], Andrea M. Bruck[b], Christopher J. Pelliccione[a], Yiman Zhang[b], Kenneth J. Takeuchi[b, c], Amy C. Marschilok[b, c], and Esther S. Takeuchi[a, b, c]

[a] Brookhaven National Laboratory, Upton, NY 11973, USA

[b] Department of Chemistry, Stony Brook University, Stony Brook, NY 11790, USA.

[c] Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY 11790, USA

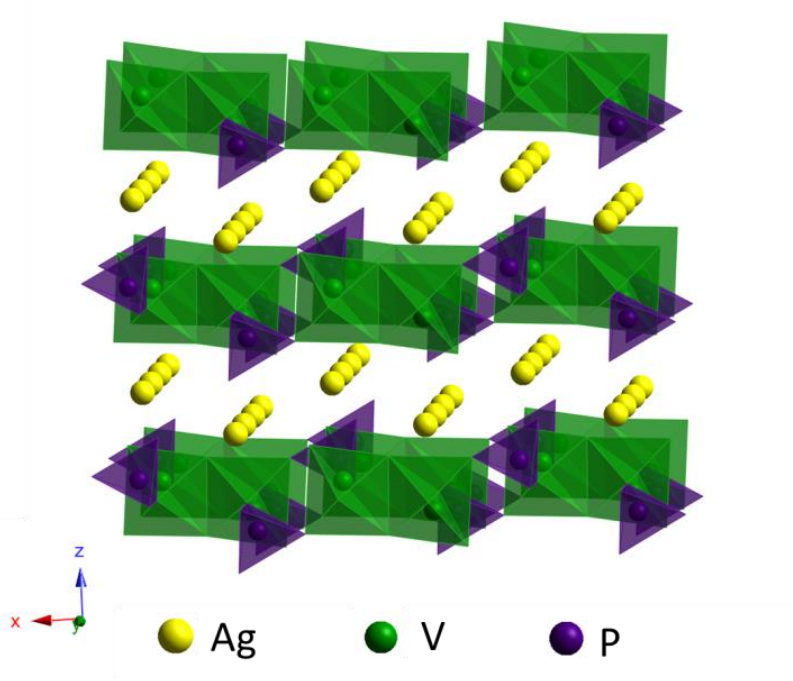

Figure S1. Crystal Structure of $Ag_2VO_2PO_4$.

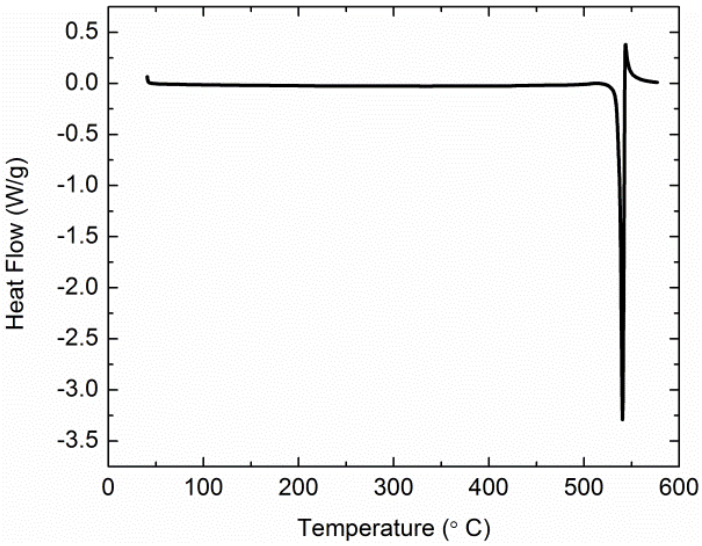

Figure S2. Differential Scanning Calorimetry of synthesized $Ag_2VO_2PO_4$.

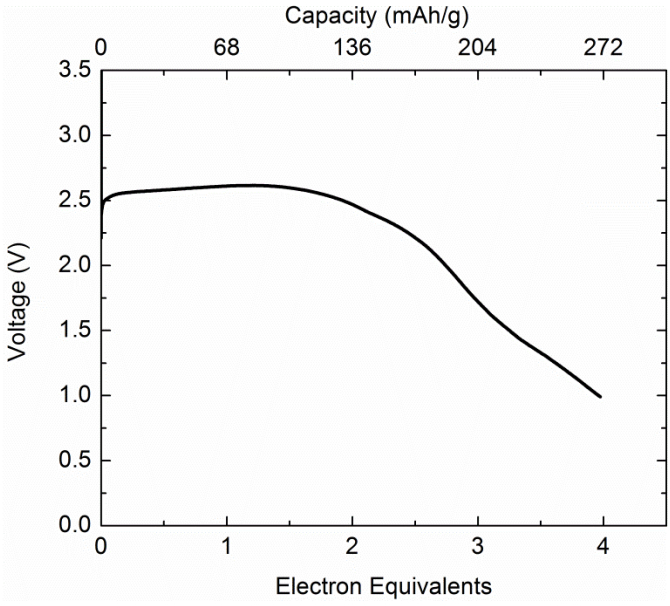

Figure S3. Constant current discharge of an $Ag_2VO_2PO_4$ electrode at C/500 rate.

Cathode Type	# e	Chi-Sqr	R_1	R_1 (Error)	R_2	R_2 (Error)	R_3	R_3 (Error)	Wo_1-R	Wo_1-R (Error)	Wo_1-T	Wo_1-T (Error)	Wo_1-P	Wo_1-P (Error)
$Ag_2VO_2PO_4$	0	0.00143	5.69	0.049	24.06	1.13	5.35E+05	4790	200	N/A	100	N/A	0.35	N/A
$Ag_2VO_2PO_4$	0.08	0.0008	4.337	0.026	47.95	1.05	155.3	1.88	155.3	1.88	126.1	7.2	0.4	0.003
$Ag_2VO_2PO_4$	0.2	0.000144	3.606	0.012	15.78	0.21	22.52	0.5099	121.1	1.9	40.9	1.2	0.33	0.0014
$Ag_2VO_2PO_4$	0.5	0.00133	2.096	0.016	11.93	0.555	8.203	1.14	47.34	2.462	37.65	3.5	0.352	0.004
$Ag_2VO_2PO_4$ + PTFE	0	0.0026	4.96	0.053	24.85	1.99	5.43E+05	7403	200	N/A	100	N/A	0.35	N/A
$Ag_2VO_2PO_4$ + PTFE	0.08	0.0001	6.78	0.015	36.48	1.48	189.1	1.991	435.7	5.9117	90.77	1.855	0.4066	0.002
$Ag_2VO_2PO_4$ + PTFE	0.2	0.000573	5.125	0.026	25.58	4.37	42.29	4.126	100.5	2.726	40.51	1.582	0.411	0.002
$Ag_2VO_2PO_4$ + PTFE	0.5	0.00045	4.569	0.028	19.83	2.4805	28.06	2.2791	89.52	2.3138	94.75	3.777	0.3948	0.00367
$Ag_2VO_2PO_4$ + PTFE + C	0	0.0067	1.908	0.0566	42	0.34	8017	511	200	N/A	100	N/A	0.35	N/A
$Ag_2VO_2PO_4$ + PTFE + C	0.08	0.000081	2.281	0.0147	28	0.205	4.342	0.35	31.59	0.798	0.656	0.017	0.4719	0.0019
$Ag_2VO_2PO_4$ + PTFE + C	0.2	0.0058	1.876	0.023	21.84	0.2	15	19	1436	200	67	11	0.51	0.03
$Ag_2VO_2PO_4$ + PTFE + C	0.5	0.0018	1.537	0.0137	18.05	0.49	5.687	2.59	57.69	3.27	24.45	2.93	0.38	0.004

Table S4. Tabulated Equivalent Circuit Fit Results for EIS data.

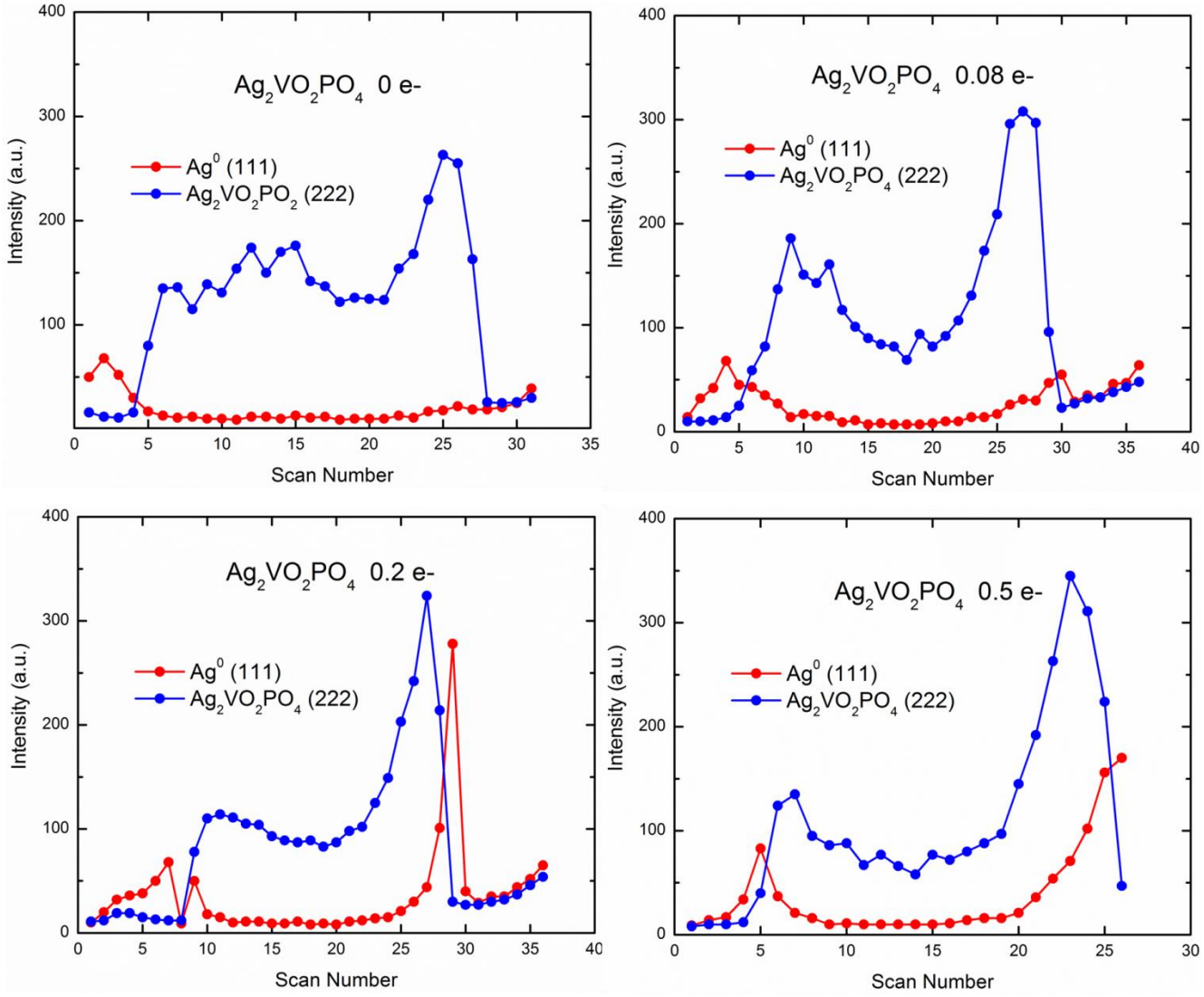

Figure S5. Ag^0 (111) and $Ag_2VO_2PO_4$ (222) peak intensities vs. scan number from EDXRD scans of the cathode region in Li / $Ag_2VO_2PO_4$ cells. Scan number increases moving from the lithium interface to the current collector interface.

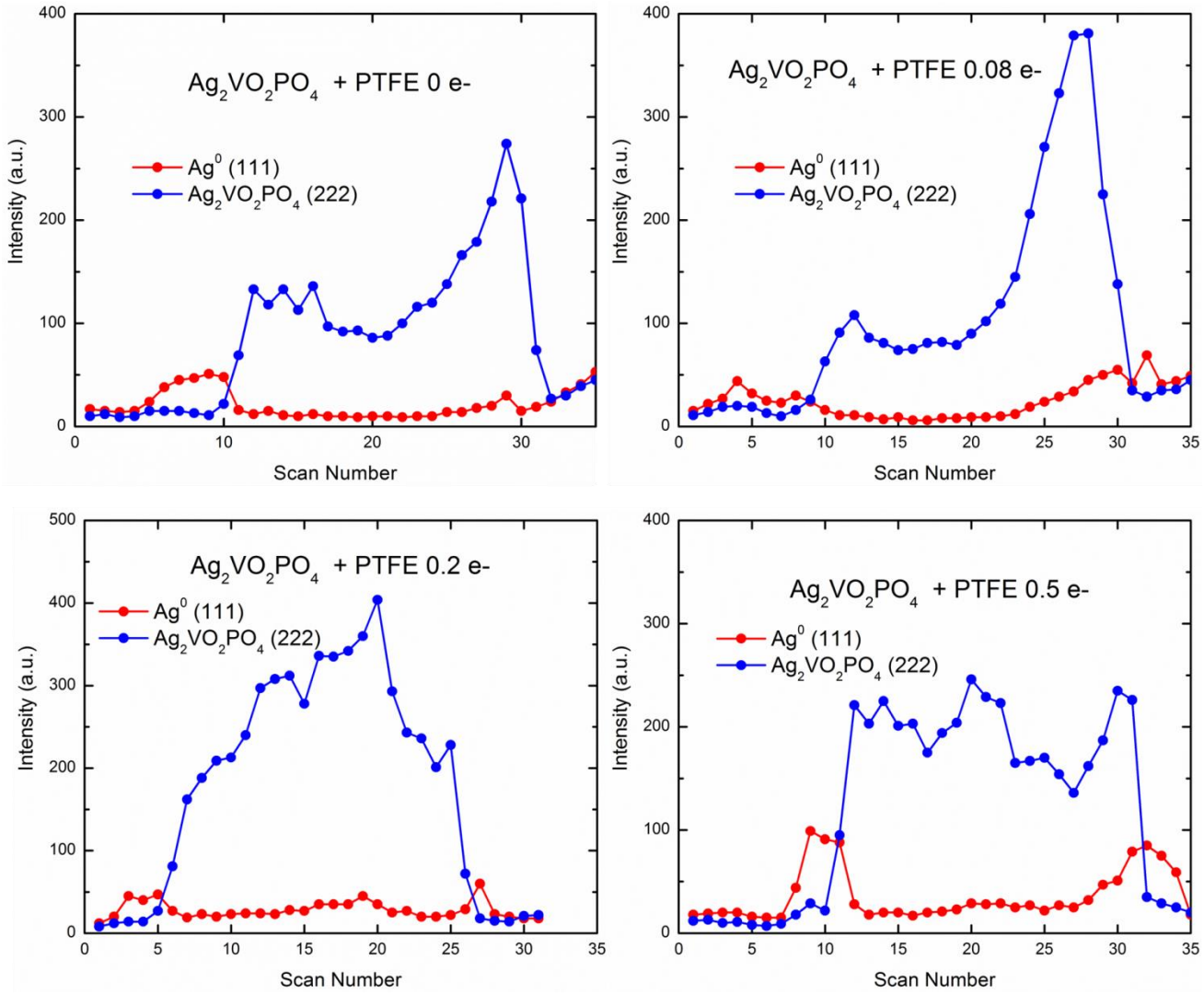

Figure S6. Ag^0 (111) and $Ag_2VO_2PO_4$ (222) peak intensities vs. scan number from EDXRD scans of the cathode region in Li / $Ag_2VO_2PO_4$ + PTFE cells. Scan number increases moving from the lithium interface to the current collector interface.

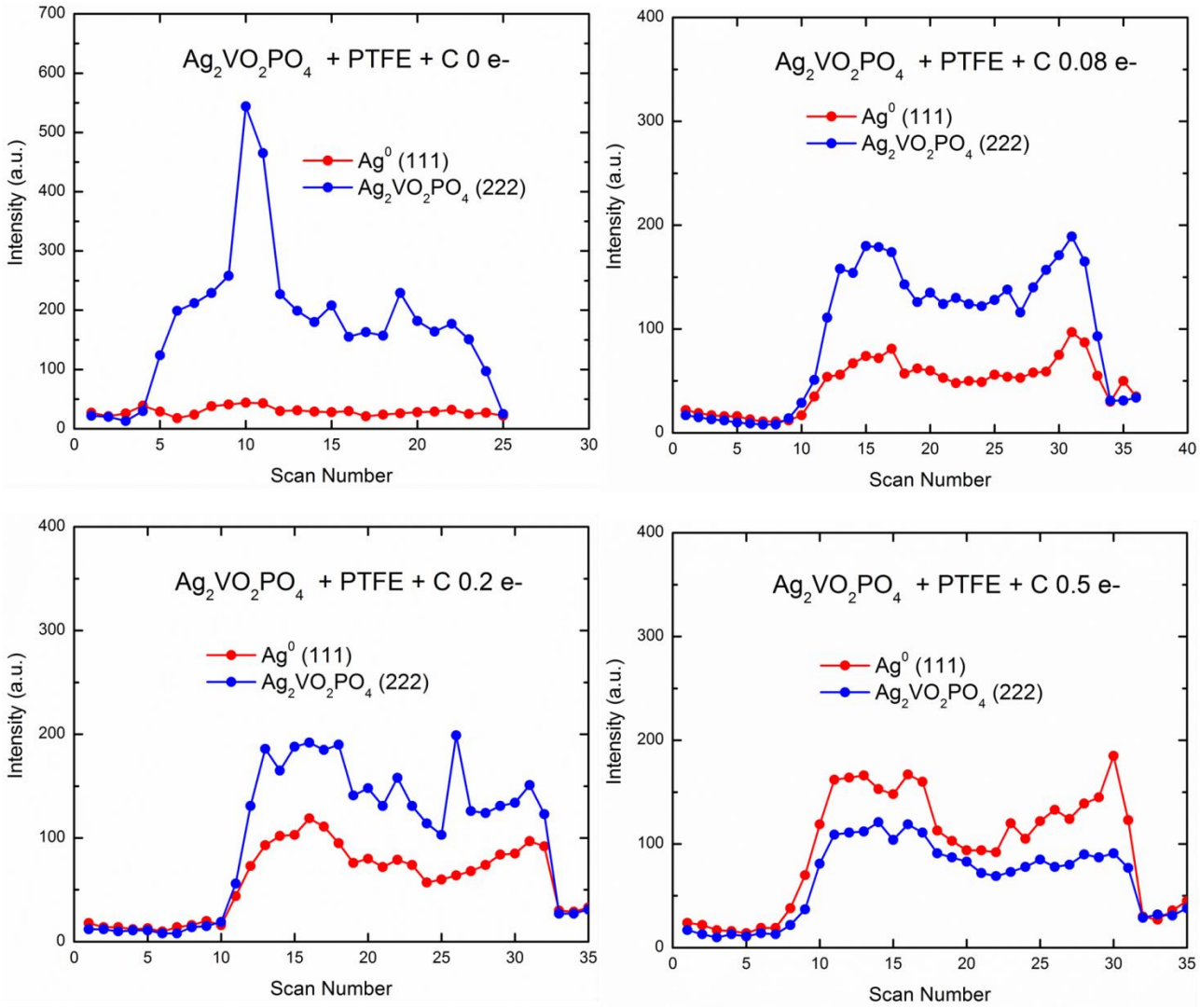

Figure S7. Ag^0 (111) and $Ag_2VO_2PO_4$ (222) peak intensities vs. scan number from EDXRD scans of the cathode region in Li / $Ag_2VO_2PO_4$ + PTFE + C cells. Scan number increases moving from the lithium interface to the current collector interface.

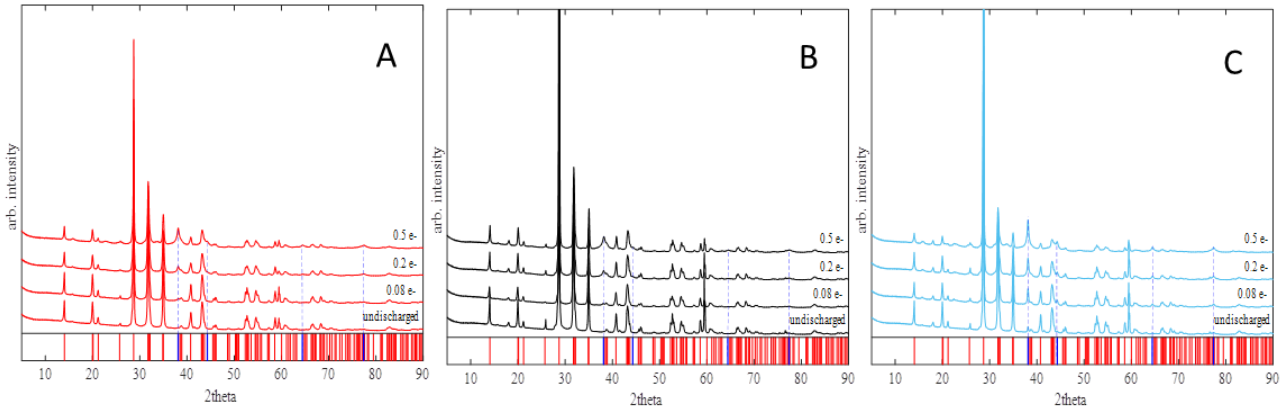

Figure S8. Ex-situ X-ray diffraction spectra for (A) $Ag_2VO_2PO_4$ only (B) $Ag_2VO_2PO_4$+PTFE and (C) $Ag_2VO_2PO_4$+PTFE+C at different levels of discharge with the red lines indicating the SVPO peaks and blue lines Ag^0.

$Ag_2VO_2PO_4$ non-discharged									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.5 ± 0.4	2.8 ± 0.8	2.8 ± 0.8	1.4 ± 0.4	1.4 ± 0.4	1.4 ± 0.4	1.4 ± 0.4	1.4 ± 0.4	-
Interatomic Distance (Å)	2.29 ± 0.07	2.61 ± 0.05	3.63 0.01	3.97 ± 0.01	3.90 ± 0.01	3.92 ± 0.01	3.66 ± 0.05	3.90 ± 0.05	-
E_o (eV)	0.3 ± 1.4	0.3 ± 1.4	0.3 ± 1.4	0.3 ± 1.4	0.3 ± 1.4	0.3 ± 1.4	0.3 ± 1.4	0.3 ± 1.4	-
Debye Waller Factor ($Å^{-2}$)	0.024 ± 0.006	0.024 ± 0.006	0.001 ± 0.006	0.001 ± 0.006	0.001 ± 0.006	0.001 ± 0.006	0.008 ± 0.007	0.008 ± 0.007	-
R-factor	1.3								
$Ag_2VO_2PO_4$ + PTFE non-discharged									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.7 ± 1.4	2.8 ± 0.7	2.8 ± 0.7	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	-
Interatomic Distance (Å)	2.31 ± 0.02	2.63 ± 0.04	3.63 ± 0.03	3.98 ± 0.03	3.91 ± 0.03	3.92 ± 0.03	3.64 ± 0.05	3.88 ± 0.05	-
E_o (eV)	0.2 ± 1.3	0.2 ± 1.3	0.2 ± 1.3	0.2 ± 1.3	0.2 ± 1.3	0.2 ± 1.3	0.2 ± 1.3	0.2 ± 1.3	-
Debye Waller Factor ($Å^{-2}$)	0.025 ± 0.005	0.25 ± 0.005	0.002 ± 0.005	0.002 ± 0.005	0.002 ± 0.005	0.002 ± 0.005	0.008 ± 0.006	0.008 ± 0.006	-
R-factor	1.6								
$Ag_2VO_2PO_4$ +PTFE + C non-discharged									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.2 ± 1.4	2.6 ± 0.7	2.6 ± 0.7	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	-
Interatomic Distance (Å)	2.31 ± 0.02	2.63 ± 0.05	3.63 ± 0.03	3.98 ± 0.03	3.91 ± 0.03	3.92 ± 0.03	3.67 ± 0.05	3.91 ± 0.05	-
E_o (eV)	0.9 ± 1.5	0.9 ± 1.5	0.9 ± 1.5	0.9 ± 1.5	0.9 ± 1.5	0.9 ± 1.5	0.9 ± 1.5	0.9 ± 1.5	-
Debye Waller Factor ($Å^{-2}$)	0.023 ± 0.005	0.023 ± 0.005	0.001 ± 0.006	0.001 ± 0.006	0.001 ± 0.006	0.001 ± 0.006	0.008 ± 0.008	0.008 ± 0.008	-
R-factor	1.7								

Table S9. EXAFS fitting results including near neighbors, interatomic distance, energy shift E_o, Debye Waller factor, and R-factor for nondischarged electrodes.

$Ag_2VO_2PO_4$ 0.08 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	6.1 ± 1.8	3.2 ± 1.0	3.2 ± 1.0	1.6 ± 0.5	1.6 ± 0.5	1.6 ± 0.5	1.6 ± 0.5	1.6 ± 0.5	-
Interatomic Distance (Å)	2.31 ± 0.03	2.64 ± 0.05	3.64 ± 0.03	3.99 ± 0.03	3.92 ± 0.03	3.93 ± 0.03	3.59 ± 0.03	3.83 ± 0.03	-
E_o (eV)	-0.3 ± 1.6	-0.3 ± 1.6	-0.3 ± 1.6	-0.3 ± 1.6	-0.3 ± 1.6	-0.3 ± 1.6	-0.3 ± 1.6	-0.3 ± 1.6	-
Debye Waller Factor ($Å^{-2}$)	0.027 ± 0.006	0.027 ± 0.006	0.010 ± 0.005	0.010 ± 0.005	0.010 ± 0.005	0.010 ± 0.005	0.010 ± 0.005	0.010 ± 0.005	-
R-factor	1.8								
$Ag_2VO_2PO_4$ + PTFE 0.08 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.4 ± 1.4	2.8 ± 0.7	2.8 ± 0.7	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	-
Interatomic Distance (Å)	2.29 ± 0.02	2.62 ± 0.05	3.63 ± 0.03	3.97 ± 0.03	3.91 ± 0.03	3.92 ± 0.03	3.57 ± 0.03	3.81 ± 0.03	-
E_o (eV)	-0.1 ± 1.5	-0.1 ± 1.5	-0.1 ± 1.5	-0.1 ± 1.5	-0.1 ± 1.5	-0.1 ± 1.5	-0.1 ± 1.5	-0.1 ± 1.5	-
Debye Waller Factor ($Å^{-2}$)	0.026 ± 0.005	0.026 ± 0.005	0.007 ± 0.006	0.007 ± 0.006	0.007 ± 0.006	0.007 ± 0.006	0.014 ± 0.010	0.014 ± 0.010	-
R-factor	1.7								
$Ag_2VO_2PO_4$ + PTFE + C 0.08 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.6 ± 1.3	2.8 ± 0.6	2.8 ± 0.6	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	0.5 ± 0.2
Interatomic Distance (Å)	2.31 ± 0.02	2.64 ± 0.05	3.64 ± 0.03	3.99 ± 0.03	3.93 ± 0.03	3.94 ± 0.03	3.59 ± 0.03	3.83 ± 0.03	2.87 ± 0.03
E_o (eV)	0.1 ± 1.3	0.1 ± 1.3	0.1 ± 1.3	0.1 ± 1.3	0.1 ± 1.3	0.1 ± 1.3	0.1 ± 1.3	0.1 ± 1.3	0.1 ± 1.3
Debye Waller Factor ($Å^{-2}$)	0.027 ± 0.004	0.001 ± 0.003	0.001 ± 0.003	0.001 ± 0.003	0.001 ± 0.003	0.001 ± 0.003	0.001 ± 0.003	0.001 ± 0.003	0.001 ± 0.003
R-factor	1.4								

Table S10. EXAFS fitting results including number of near neighbors, interatomic distance, energy shift E_o, Debye Waller factor, and R-factor for electrodes discharged to 0.08 electron equivalents.

$Ag_2VO_2PO_4$ 0.2 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.8 ± 1.4	2.8 ± 0.7	2.8 ± 0.7	1.4 ± 0.4	1.4 ± 0.4	1.4 ± 0.4	1.4 ± 0.4	1.4 ± 0.4	0.5 ± 0.3
Interatomic Distance (Å)	2.31 ± 0.02	2.64 ± 0.05	3.65 ± 0.03	3.99 ± 0.03	3.93 ± 0.03	3.94 ± 0.03	3.6 ± 0.03	3.84 ± 0.03	2.87 ± 0.03
E_o (eV)	0.1 ± 1.4	0.1 ± 1.4	0.1 ± 1.4	0.1 ± 1.4	0.1 ± 1.4	0.1 ± 1.4	0.1 ± 1.4	0.1 ± 1.4	0.1 ± 1.4
Debye Waller Factor ($Å^{-2}$)	0.028 ± 0.005	0.028 ± 0.005	0.010 ± 0.004	0.010 ± 0.004	0.010 ± 0.004	0.010 ± 0.004	0.010 ± 0.004	0.010 ± 0.004	0.010 ± 0.004
R-factor	1.6								
$Ag_2VO_2PO_4$ + PTFE 0.2 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.5 ± 1.1	2.8 ± 0.5	2.8 ± 0.5	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	0.5 ± 0.3
Interatomic Distance (Å)	2.31 ± 0.02	2.64 ± 0.05	3.63 ± 0.03	3.97 ± 0.03	3.91 ± 0.03	3.92 ± 0.03	3.58 ± 0.03	3.82 ± 0.03	2.85 ± 0.03
E_o (eV)	-0.2 ± 1.0	-0.2 ± 1.0	-0.2 ± 1.0	-0.2 ± 1.0	-0.2 ± 1.0	-0.2 ± 1.0	-0.2 ± 1.0	-0.2 ± 1.0	-0.2 ± 1.0
Debye Waller Factor ($Å^{-2}$)	0.026 ± 0.004	0.026 ± 0.004	0.009 ± 0.004	0.009 ± 0.004	0.009 ± 0.004	0.009 ± 0.004	0.009 ± 0.004	0.009 ± 0.004	0.009 ± 0.004
R-factor	1.3								
$Ag_2VO_2PO_4$ + PTFE + C 0.2 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.5 ± 1.3	2.8 ± 0.6	2.8 ± 0.6	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	0.9 ± 0.3
Interatomic Distance (Å)	2.32 ± 0.02	2.65 ± 0.02	3.66 ± 0.03	4.00 ± 0.03	3.94 ± 0.03	3.95 ± 0.03	3.61 ± 0.03	3.85 ± 0.03	2.88 ± 0.02
E_o (eV)	0.3 ± 1.2	0.3 ± 1.2	0.3 ± 1.2	0.3 ± 1.2	0.3 ± 1.2	0.3 ± 1.2	0.3 ± 1.2	0.3 ± 1.2	0.3 ± 1.2
Debye Waller Factor ($Å^{-2}$)	0.027 ± 0.005	0.008 ± 0.008	0.008 ± 0.008	0.008 ± 0.008	0.008 ± 0.008	0.008 ± 0.008	0.008 ± 0.008	0.008 ± 0.008	0.008 ± 0.008
R-factor	1.6								

Table S11. EXAFS fitting results including number of near neighbors, interatomic distance, energy shift E_o, Debye Waller factor, and R-factor for electrodes discharged to 0.2 electron equivalents.

$Ag_2VO_2PO_4$ 0.5 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.0 ± 1.4	2.6 ± 0.7	2.6 ± 0.7	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	2.1 ± 0.5
Interatomic Distance (Å)	2.33 ± 0.03	2.66 ± 0.04	3.64 ± 0.04	3.99 ± 0.04	3.93 ± 0.04	3.94 ± 0.04	3.59 ± 0.04	3.83 ± 0.04	2.87 ± 0.01
E_o (eV)	0.5 ± 1.2	0.5 ± 1.2	0.5 ± 1.2	0.5 ± 1.2	0.5 ± 1.2	0.5 ± 1.2	0.5 ± 1.2	0.5 ± 1.2	0.5 ± 1.2
Debye Waller Factor ($Å^{-2}$)	0.028 ± 0.006	0.011 ± 0.003	0.011 ± 0.003	0.011 ± 0.003	0.011 ± 0.003	0.011 ± 0.003	0.011 ± 0.003	0.011 ± 0.003	0.011 ± 0.003
R-factor	1.6								
$Ag_2VO_2PO_4$ + PTFE 0.5 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	5.1 ± 1.4	2.6 ± 0.7	2.6 ± 0.7	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	1.3 ± 0.4	1.7 ± 0.5
Interatomic Distance (Å)	2.32 ± 0.03	2.66 ± 0.04	3.64 ± 0.04	3.98 ± 0.04	3.92 ± 0.04	3.93 ± 0.04	3.58 ± 0.04	3.82 ± 0.04	2.87 ± 0.01
E_o (eV)	0.4 ± 1.4	0.4 ± 1.4	0.4 ± 1.4	0.4 ± 1.4	0.4 ± 1.4	0.4 ± 1.4	0.4 ± 1.4	0.4 ± 1.4	0.4 ± 1.4
Debye Waller Factor ($Å^{-2}$)	0.028 ± 0.006	0.028 ± 0.006	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003
R-factor	2.0								
$Ag_2VO_2PO_4$ + PTFE + C 0.5 e									
Path	**Ag-O path 1 (SVPO)**	**Ag-O path 2 (SVPO)**	**Ag-O path 3 (SVPO)**	**Ag-O path 4 (SVPO)**	**Ag-P (SVPO)**	**Ag-V (SVPO)**	**Ag-Ag path 1 (SVPO)**	**Ag-Ag path 2 (SVPO)**	**Ag-Ag (fcc metal)**
Near Neighbors	4.4 ± 1.5	1.2 ± 0.8	1.2 ± 0.8	1.1 ± 0.4	1.1 ± 0.4	1.1 ± 0.4	1.1 ± 0.4	1.1 ± 0.4	2.4 ± 0.5
Interatomic Distance (Å)	2.32 ± 0.04	2.62 ±0.09	3.62 ± 0.05	3.97 ± 0.05	3.90 ± 0.05	3.92 ± 0.05	3.58 ± 0.05	3.81 ± 0.05	2.85 ± 0.01
E_o (eV)	-0.7 ± 1.3	-0.7 ± 1.3	-0.7 ± 1.3	-0.7 ± 1.3	-0.7 ± 1.3	-0.7 ± 1.3	-0.7 ± 1.3	-0.7 ± 1.3	-0.7 ± 1.3
Debye Waller Factor ($Å^{-2}$)	0.025 ± 0.007	0.025 ± 0.007	0.012 ± 0.003	0.012 ± 0.003	0.012 ± 0.003	0.012 ± 0.003	0.012 ± 0.003	0.012 ± 0.003	0.012 ± 0.003
R-factor	2.6								

Table S12. EXAFS fitting results including number of near neighbors, interatomic distance, energy shift E_o, Debye Waller factor, and R-factor for electrodes discharged to 0.5 electron equivalents.

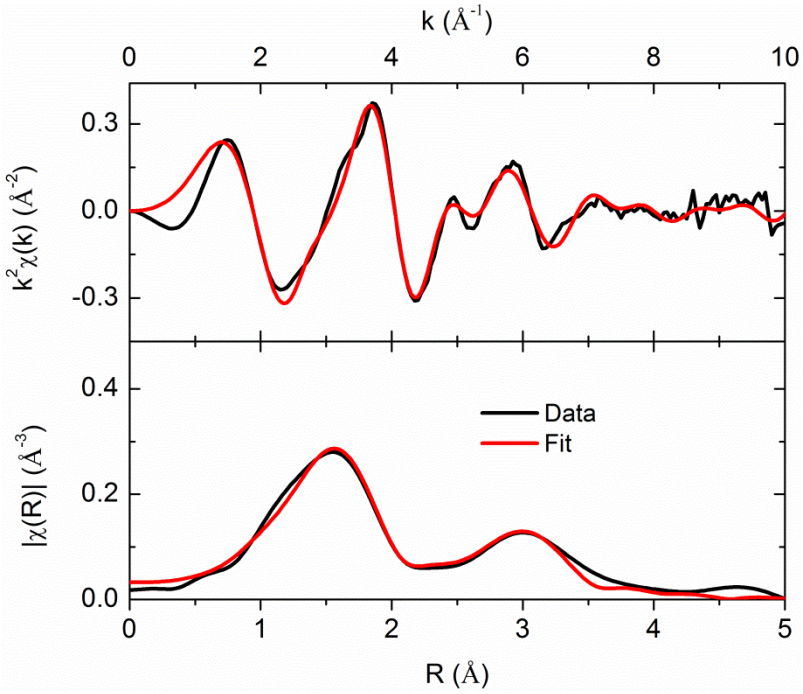

Figure S13: EXAFS fit of the undischarged state for the $Ag_2VO_2PO_4$ electrode in $|\chi(R)|$ and $k^2\chi(k)$.

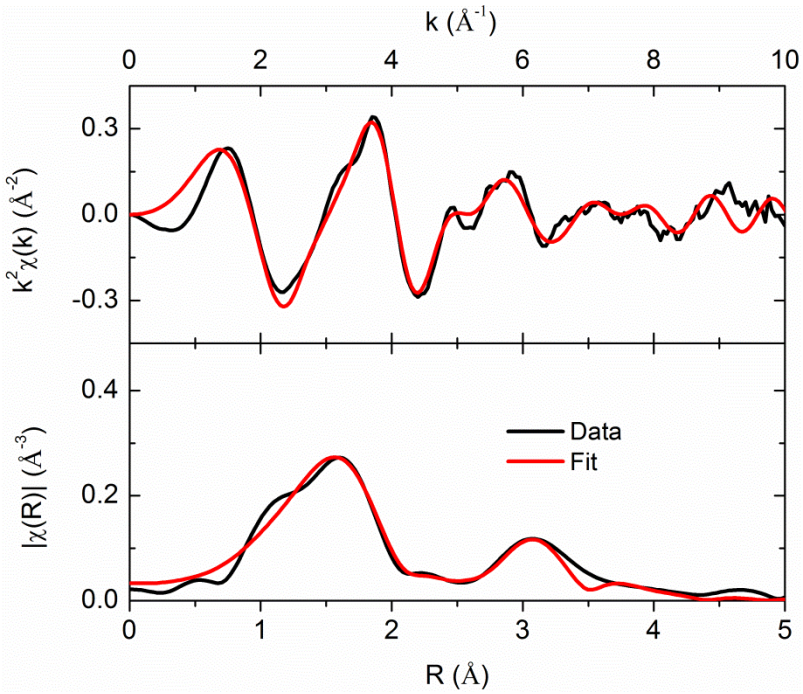

Figure S14: EXAFS fit of the $Ag_2VO_2PO_4$ electrode discharged to 0.08 electron equivalents in $|\chi(R)|$ and $k^2\chi(k)$.

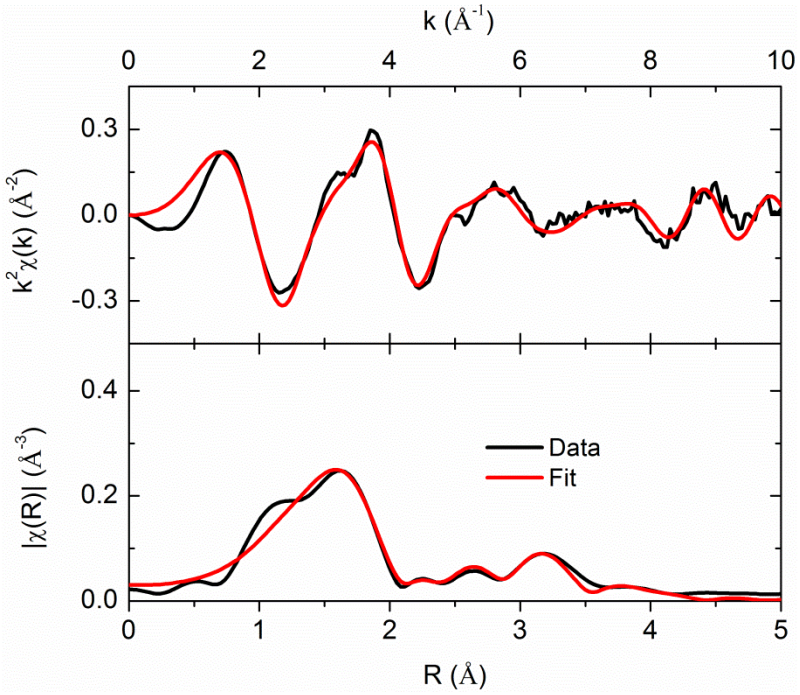

Figure S15: EXAFS fit of the $Ag_2VO_2PO_4$ electrode discharged to 0.2 electron equivalents in $|\chi(R)|$ and $k^2\chi(k)$.

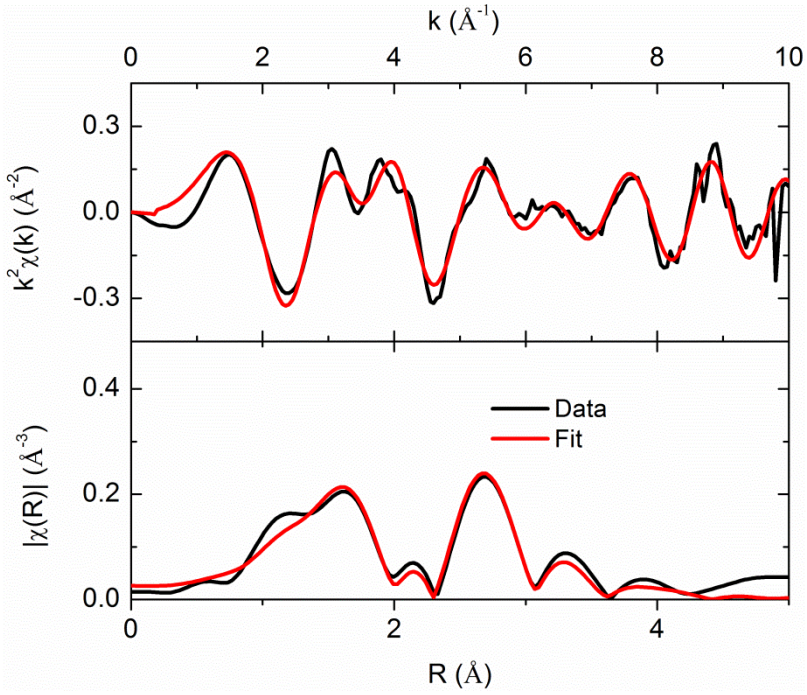

Figure S16: EXAFS fit of the $Ag_2VO_2PO_4$ electrode discharged to 0.2 electron equivalents in $|\chi(R)|$ and $k^2\chi(k)$.

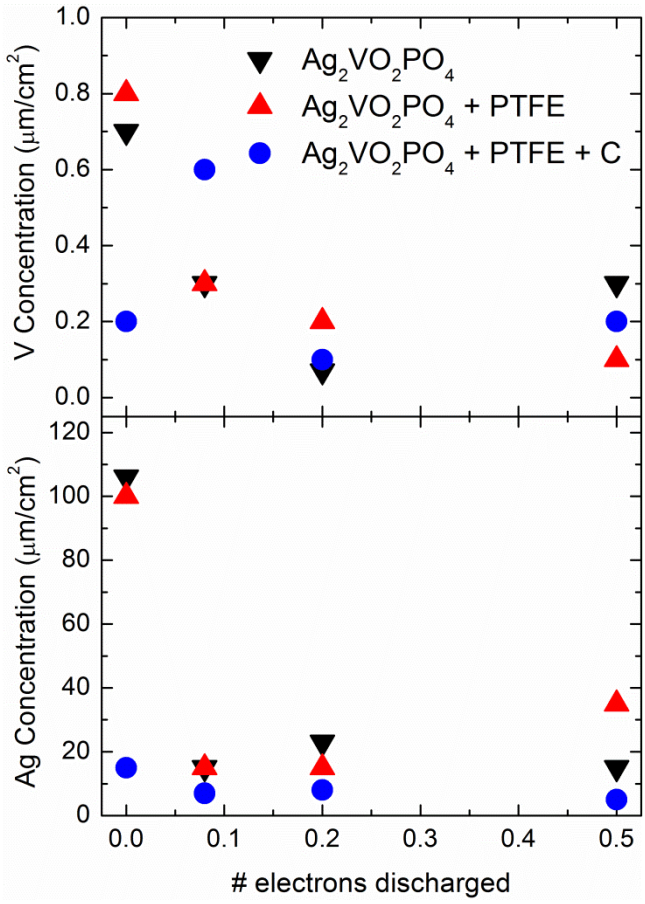

Figure S17. Quantitative analysis of lithium anodes recovered from Li/$Ag_2VO_2PO_4$.