Supporting Information

Effect of Vanadium Doping on α-K_xMnO_2 as a Positive Electrode Active Material for Rechargeable Magnesium Batteries

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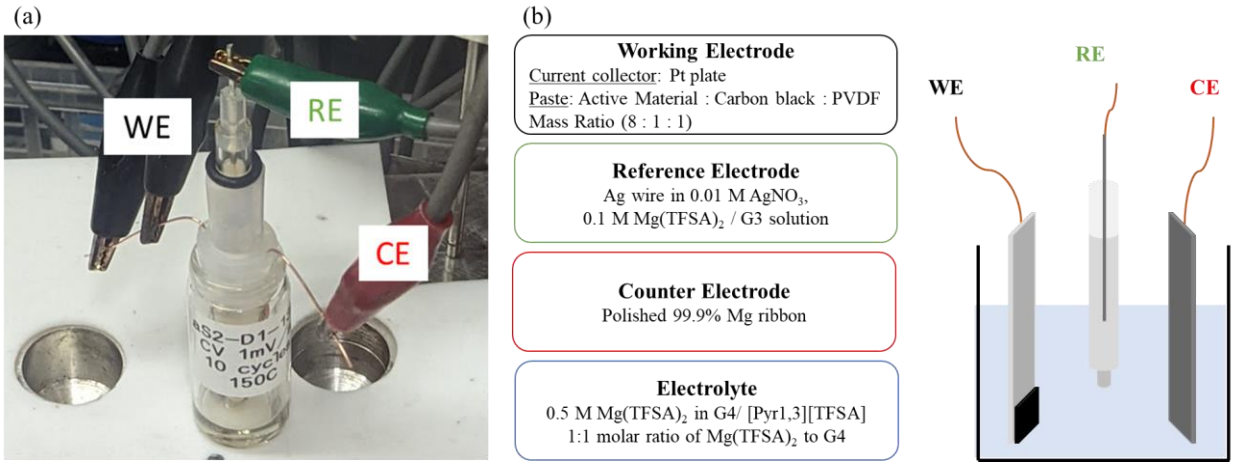

Figure S1. (a) Picture of the three-electrode beaker cell used for electrochemical measurements, (b) schematic diagram of the three-electrode beaker cell setup with details regarding individual components.

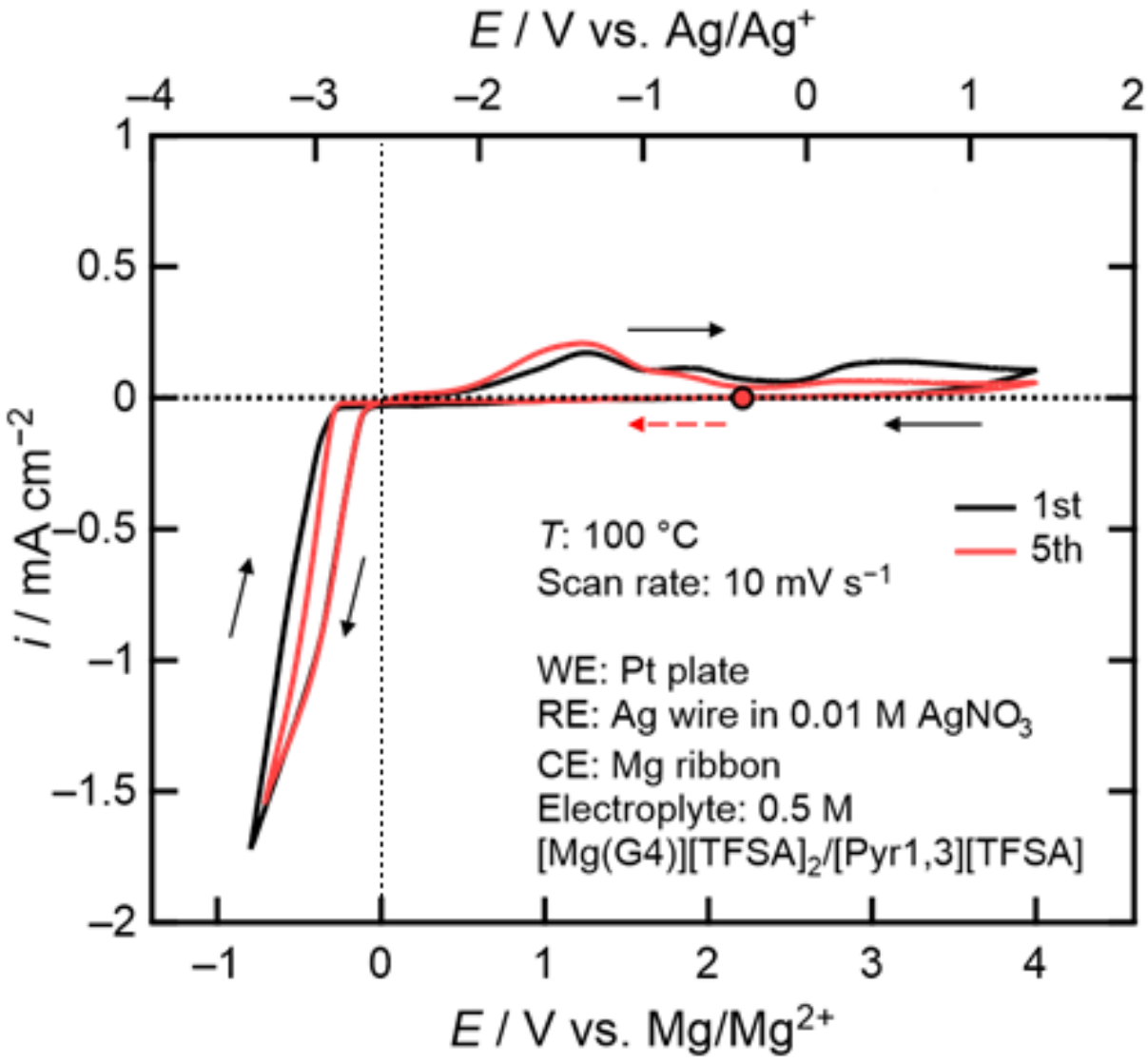

Figure S2. Cyclic voltammogram with Pt working electrode measured at a scan rate 10 mV s^{-1} at 100 °C. The potential at which Mg deposition and dissolution were observed, denoted with the doted line above, was used to determine the conversion from the Ag/Ag^{+} reference to Mg/Mg^{2+}: 0 V *vs.* Mg/Mg^{2+} = –2.6 V *vs.* Mg/Mg^{2+}.

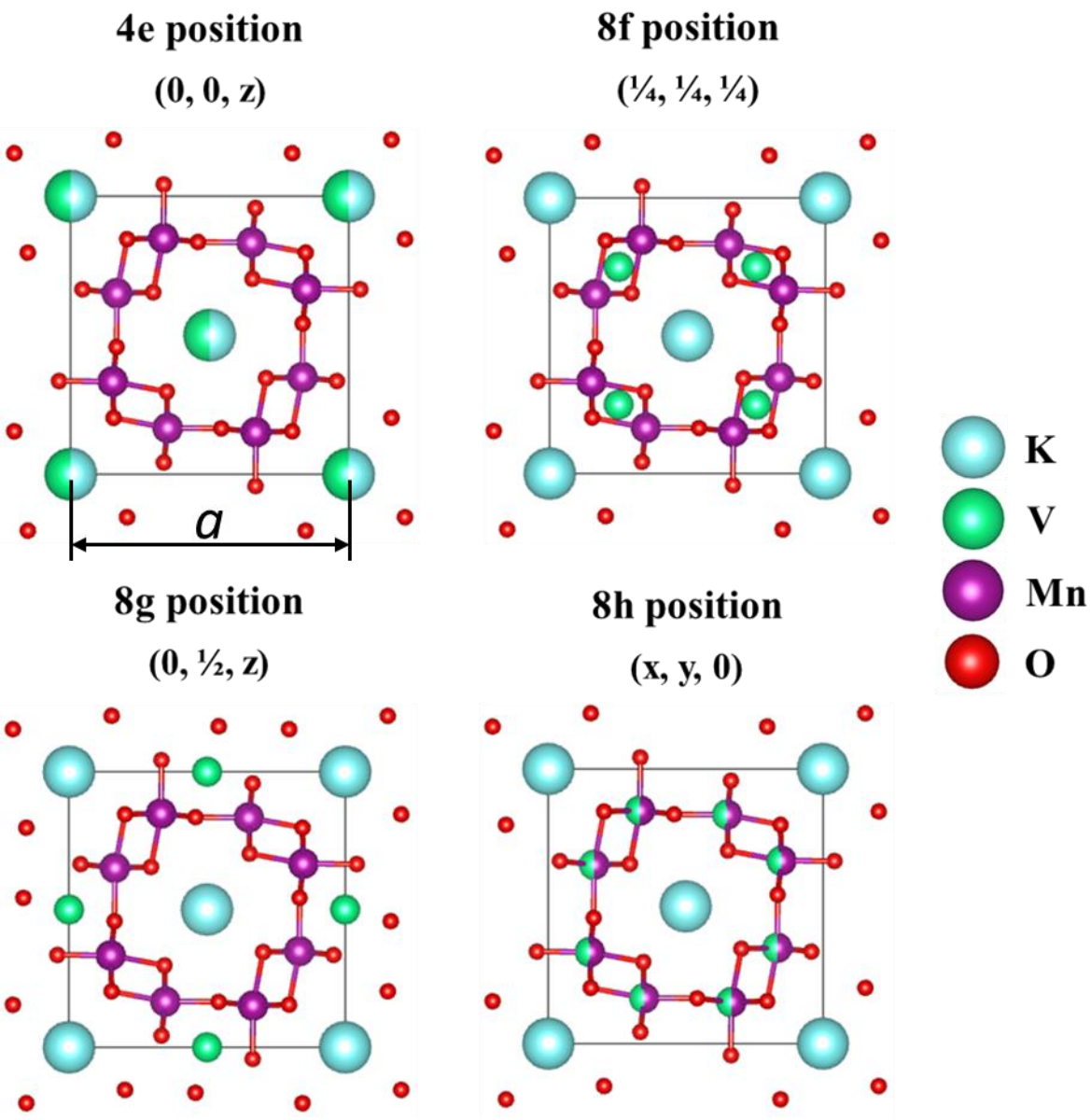

Figure S3. Diagram of Wyckoff positions tested for Vanadium addition using Rietveld refinement of SXRD profiles taken for 7.2% V-doped α-MnO_2. Refinement was carried out using the location constraints listed below each symmetry label. Mn:V ratio was constrained by the ratios observed using ICP spectroscopy measurements. Rietveld Refinement was conducted for four iterations and the most likely geometry was determined by the reliability-weighted pattern factor (R_{wp}) indicating the fit of the calculated structure with the measured SXRD peak profile. The lattice parameter *a* is labeled in the top left diagram.

Table S1. Lattice constant (a), site occupancy (g), fractional coordinate (x, y, z), and R_{wp} factors for 7.2% V-doped α-K_xMnO_2 calculated by Rietveld refinement of the 7.2% V-doped sample SXRD profile from Figure 1e using V positions constrained to the Wyckoff positions detailed in Figure S2.

Tested V-site	*a* / Å	Atom	*site*	*g*	*x*	*y*	*z*	*Rwp*
4e	9.8400	K1	2a	0.2162	0	0	0	8.309
		Mn1	8h	0.9168	0.1510	0.3330	0	
		O1		0.9954	0.3449	0.2984	0	
		O2		1 (fixed)	0.3364	0.0389	0	
		V1	4e	0.1417 (c)	0	0	0.1529	
8f	9.8395	K1	2a	0.5526	0	0	0	8.930
		Mn1	8h	0.9176	0.1500	0.3335	0	
		O1		0.9302	0.3545	0.3037	1/2	
		O2		1 (fixed)	0.3405	0.0393	1/2	
		V1	8f	0.0709 (c)	1/4	1/4	1/4	
8g	9.8398	K1	2a	0.5365	0	0	0	10.986
		Mn1	8h	0.8873	0.1496	0.3308	0	
		O1		1 (fixed)	0.3455	0.2972	0	
		O2		0.8251	0.3216	0.0396	0	
		V1	8g	0.0686 (c)	0	1/2	0.1517	
8h	9.8418	K1	2a	0.5395	0	0	0	4.587
		Mn1	8h	0.8822	0.1511	0.3332	0	
		O1		0.9793	0.3470	0.2990	0	
		O2		1 (fixed)	0.3363	0.0447	0	
		V1		0.0682 (c)	0.1513	0.3332	0	

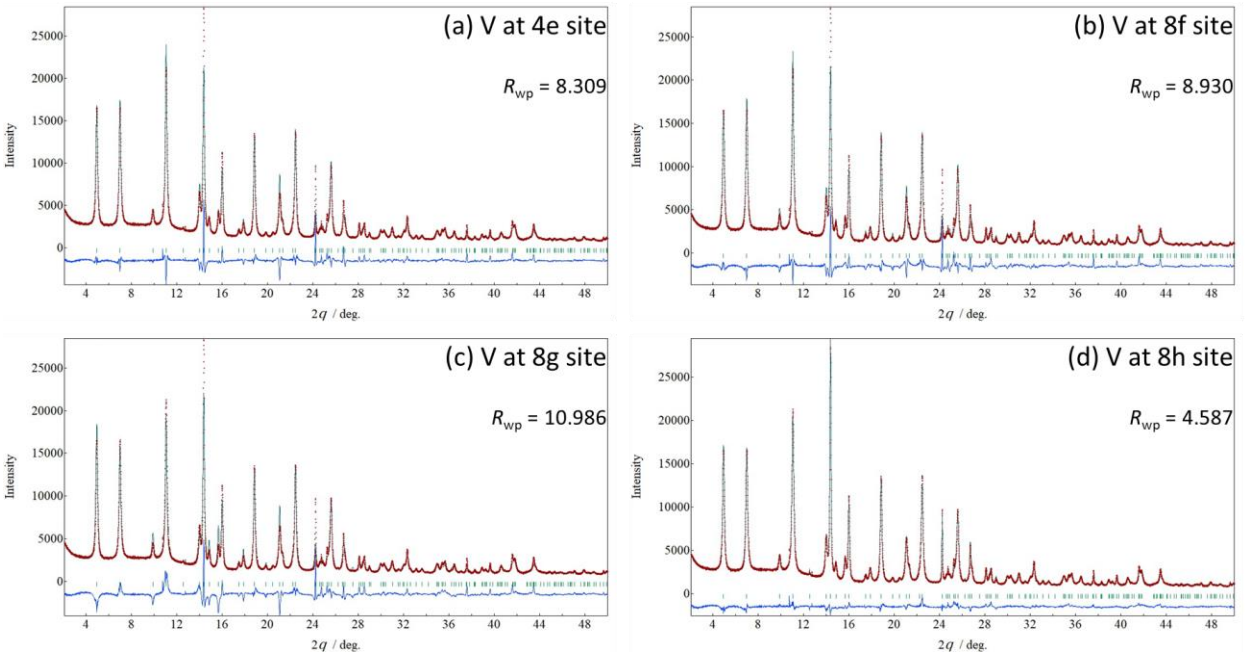

Figure S4. Synchrotron X-ray diffraction (SXRD) profiles for 7.2% V-doped α-K_xMnO_2 with Rietveld refinement fitting profiles corresponding to V positions constrained to the Wyckoff positions (a) 4e, (b) 8f, (c) 8g, and (d) 8h. The red dots indicate the measured SRXD profiles, fitting curves calculated by Rietveld refinement are in green, and the difference between the measured profiles and fitting curves are in blue. The wavelength of the irradiated X-rays was calibrated to 0.59999 Å using a CeO_2 standard sample. R_{wp} represents the reliability-weighted pattern factor for the refinement.

Table S2. Area ratios for fitting peaks calculated for Mn $2p_{3/2}$ profiles measured using X-ray photoelectron spectroscopy (XPS) for undoped and 7.2% V-doped α-K_xMnO_2. Calculated average valences are within errors expected for XPS. Mn^{3+} (MnOOH) represents hydrated Mn^{3+} species on the surface of the sample.

Fitting curve	**Undoped α-K_xMnO_2**		**7.2% V-doped α-K_xMnO_2**	
	Area	**Percentage**	**Area**	**Percentage**
Mn^{3+}	5491	23.1%	6062	20.5%
Mn^{4+}	12314	51.8%	16114	54.5%
Mn^{3+} sat.	3798	16.0%	3875	13.1%
Mn^{4+} sat.	1374	5.8%	2220	7.5%
Mn^{3+} (MnOOH)	791	3.3%	1308	4.4%
Average valence	3.58		3.62	
Chi squared	3.46		3.35	

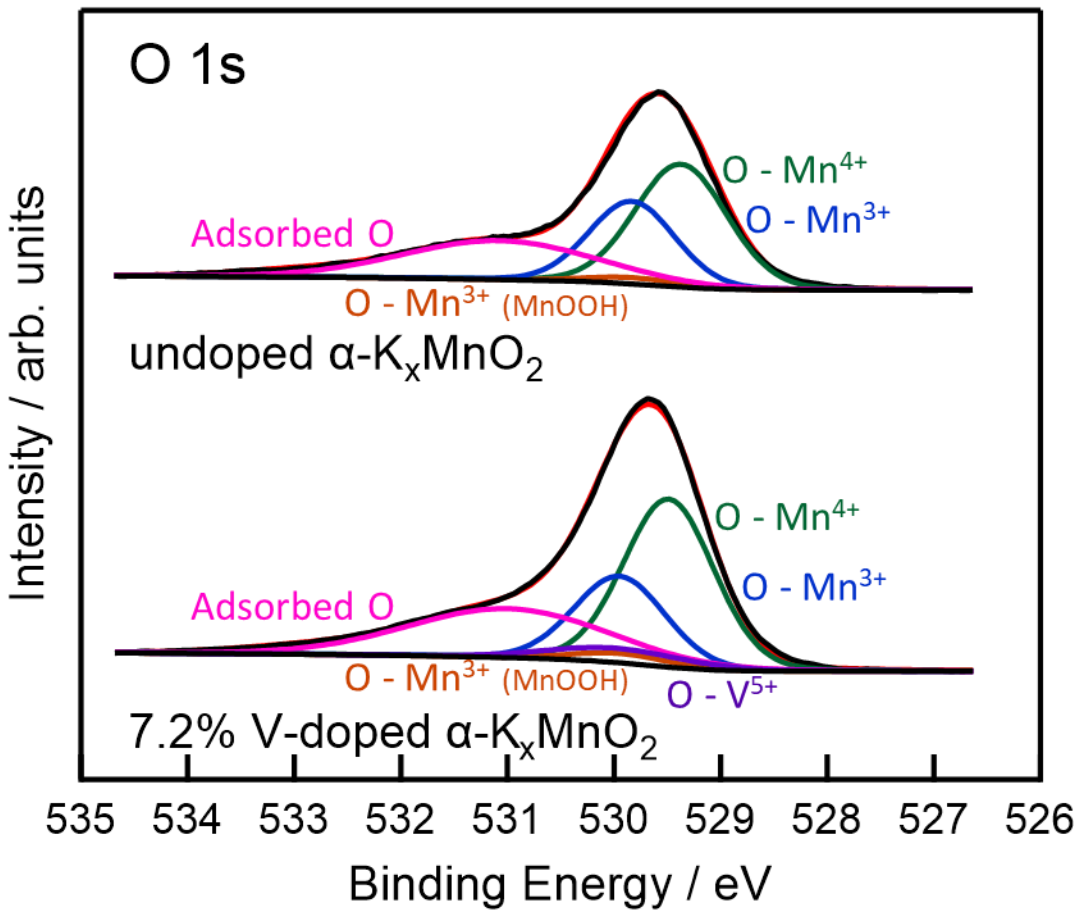

Figure S5. XPS fitting profiles for undoped and 7.2% V-doped α-K_xMnO_2 O 1s profiles. Area ratios of O-*M* bonds determined by area ratios from Mn 2p profiles. The O-V^{5+} area ratio is determined by ICP concentration ratio. XPS profiles were aligned using a peak position of 284.8 eV for adventitious carbon within the C 1s profile.

Table S3. Area ratios of fitting peaks calculated for O 1s profiles measured using X-ray photoelectron spectroscopy for undoped and 7.2% V-doped α-K_xMnO_2.

Oxygen Type	**Fitting Curve Descriptor**	**Undoped α-K_xMnO_2**		**7.2% V-doped α-K_xMnO_2**	
		Area	**Percentage**	**Area**	**Percentage**
Lattice Oxygen	O - Mn^{4+}	7049	42.4%	9433	42.5%
	O - Mn^{3+}	4441	26.8%	4934	22.2 %
	O - V^{5+}	-	-	1161	5.2%
Surface Oxygen	Adsorbed O	4724	28.4%	6120	27.6%
	Mn^{3+} (MnOOH)	374	2.3%	566	2.5%
Chi Squared		3.59		2.07	

Table S4. Atomic ratios of K, Mn, V, and O classified by atomic species calculated from XPS profiles measured for undoped and 7.2% V-doped α-K_xMnO_2, respectively.

Element	Undoped α-K_xMnO_2	7.2% V-doped α-K_xMnO_2
K	3.8	4.1
Mn	32.5	30.3
V	-	2.5
O	63.7	63.0

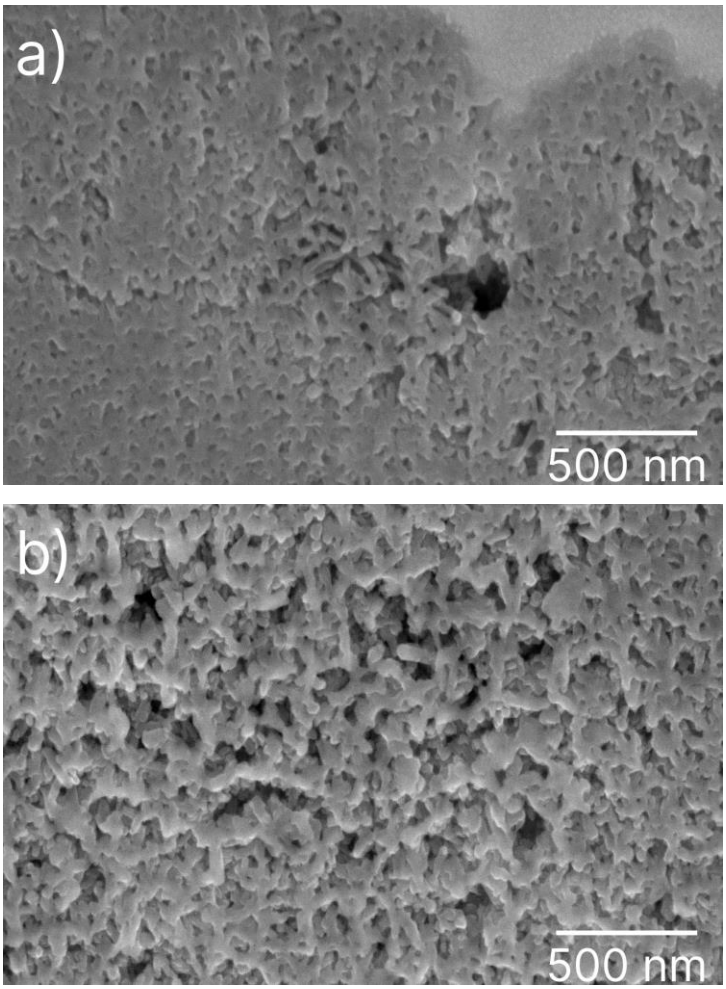

Figure S6. (a) High-resolution SEM image of undoped α-K_xMnO_2 cross section. (b) High-resolution SEM image of 7.2% V-doped α-K_xMnO_2 cross section. Both samples are composed by aggregation of the small capsule-shaped grains. Both samples experienced deformation upon FIB cutting despite the use of a Pt protective layer.

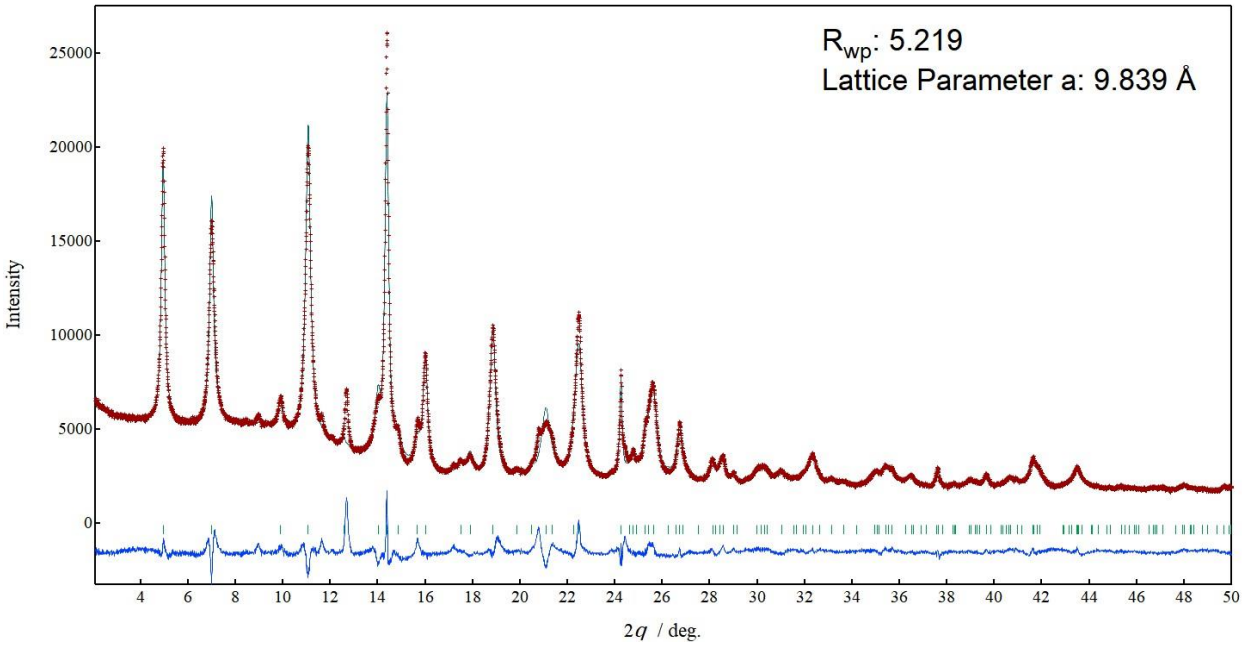

Figure S7. Rietveld Refinement of undoped α-K_xMnO_2. Lattice parameter *a* was calculated at 9.839 Å. The lattice parameter for 7.2% V-doped α-K_xMnO_2 of 9.842 Å is presented in Table S1.