Supporting Information

Microwave-assisted chemical insertion: A rapid technique for screening cathodes for Mg-ion batteries

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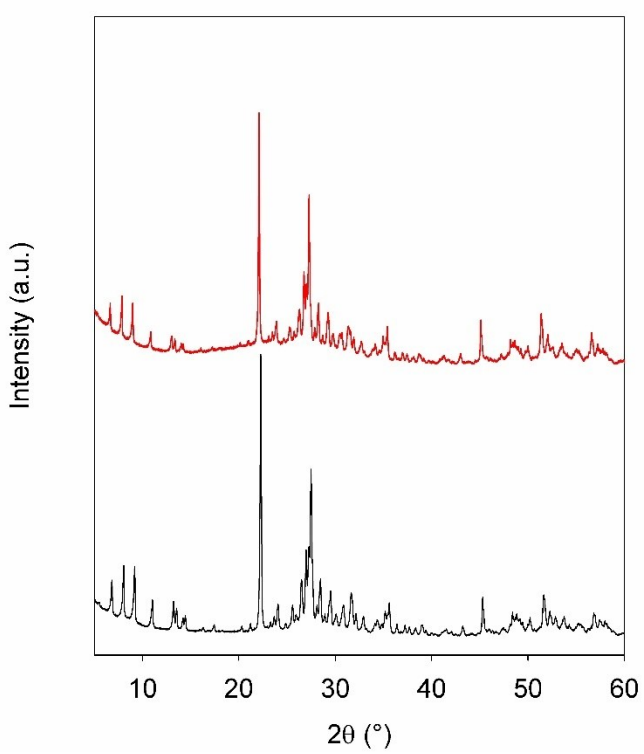


Fig. S1 Powder X-ray diffraction patterns of as-synthesized $Mo_{2.5+y}VO_{9+z}$ from microwave-assisted hydrothermal reaction (red) and microporous $Mo_{2.5+y}VO_{9+z}$ after calcination at 400 °C (black).

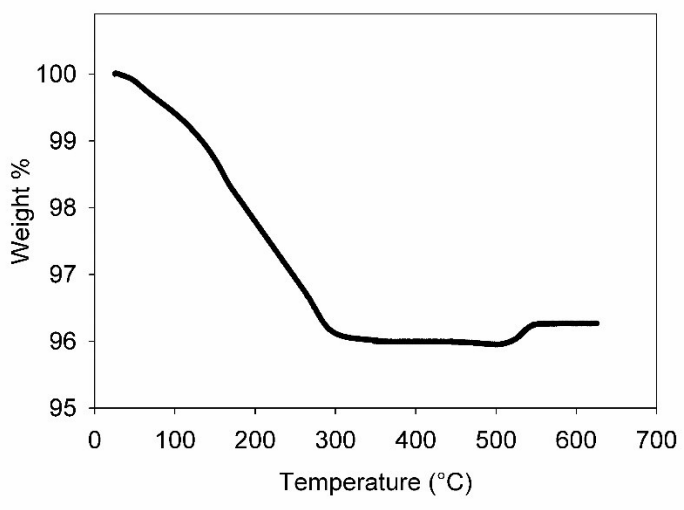
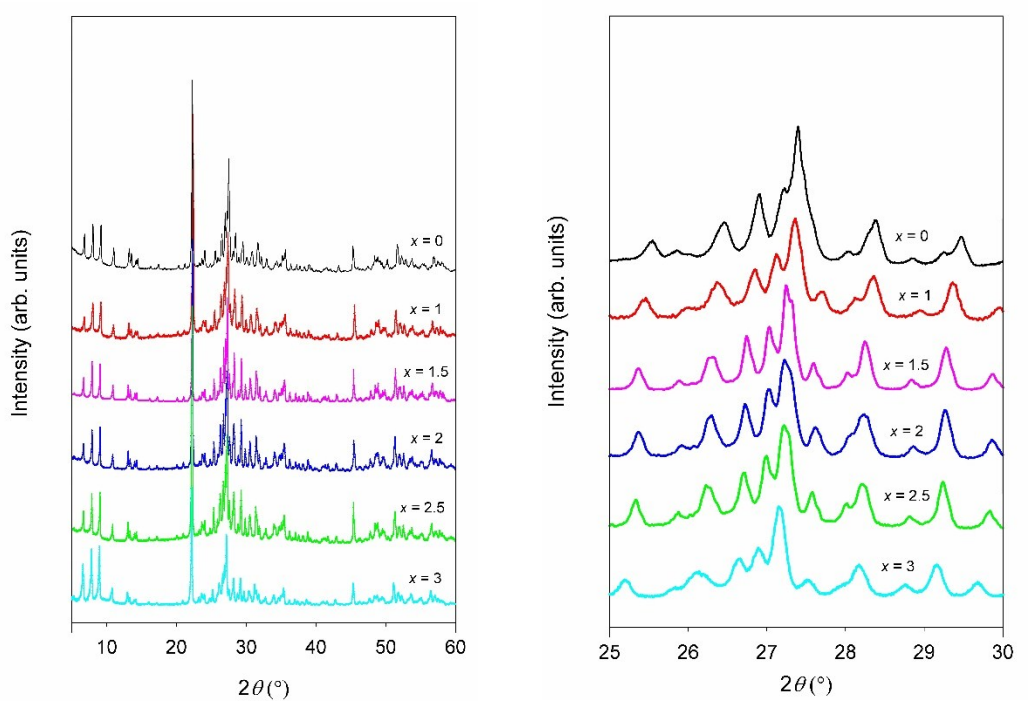


Fig. S2 Thermogravimetric analysis of the as-synthesized $Mo_{2.5+y}VO_{9+z}$ in oxygen atmosphere.



(a) (b)

Fig. S3 (a) PXRD patterns of $Mg_xMo_{2.5+y}VO_{9+z}$ ($0 \leq x \leq 3$) prepared by the microwave-assisted chemical insertion with DEG and $Mg(CH_3COO)_2$. (b) PXRD patterns at selected 2θ range (25−30°) to illustrate the changes in the peak positions.

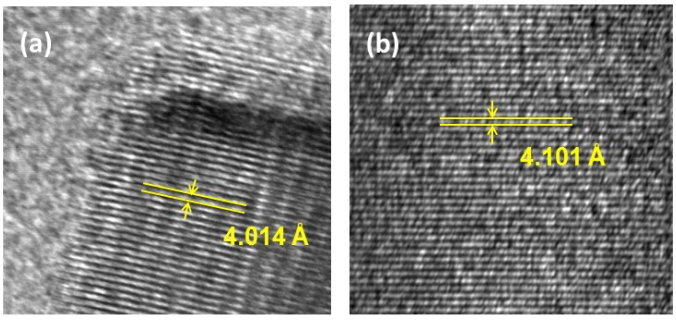


Fig. S4 HR-TEM lattice images along [001] of (a) pristine $Mg_xMo_{2.5+y}VO_{9+z}$ ($x = 0$) and (b) Mg-inserted product ($x = 2$), showing a slight expansion of the *c* parameter (layer stacking direction), which is consistent with an expansion observed by the profile fitting.

Table S1 Microwave-assisted chemical lithiation conditions and the metal contents of the Li-inserted products

Host Compound	Temperature (°C)	Hold Time (min)	LiOH Equivalent	ICP Stoichiometry Lithium : Transition Metal
$LiVOPO_4$	190	30	4	1.31 : 1
$LiVOPO_4$	210	30	4	1.55 : 1
TiO_2	190	30	2	0.48 : 1
TiO_2	210	30	2	0.62 : 1
Fe_2O_3	220	30	3	0.03 : 1
Fe_2O_3	240	30	3	0.14 : 1
Fe_2O_3	240	30	4	0.15 : 1

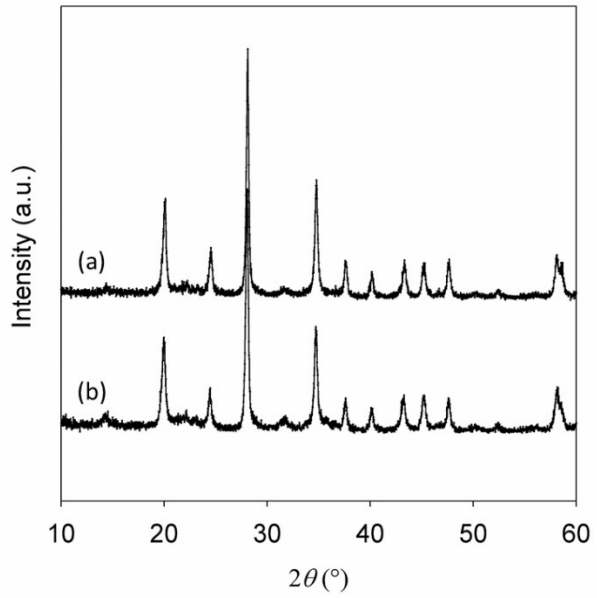


Fig. S5 PXRD patterns of Li_xVOPO_4 prepared by the microwave-assisted chemical insertion: (a) $x = 1.31$ and (b) $x = 1.55$.

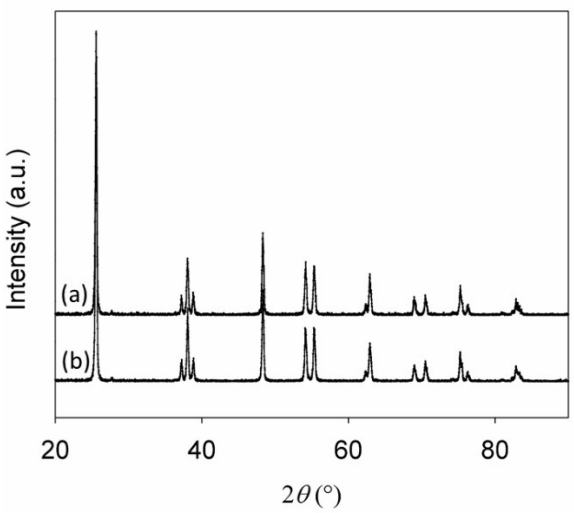


Fig. S6 PXRD patterns of Li_xTiO_2 prepared by the microwave-assisted chemical insertion: (a) x = 0.48 and (b) x = 0.62.

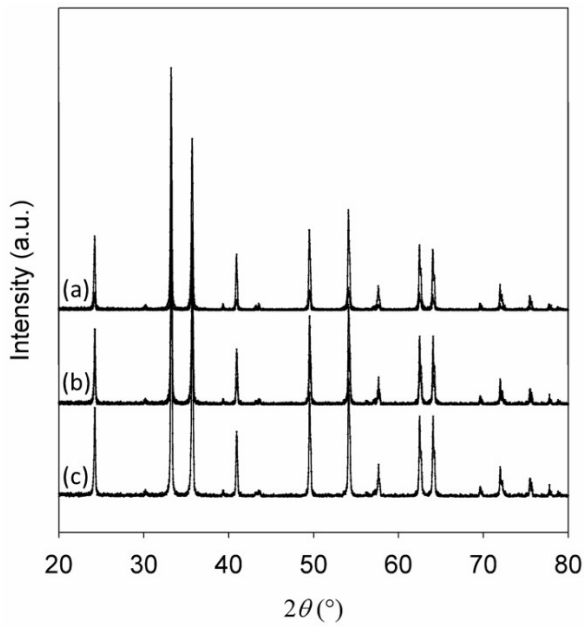
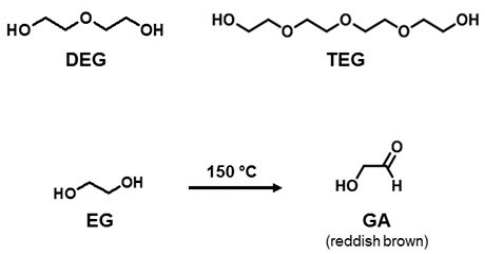
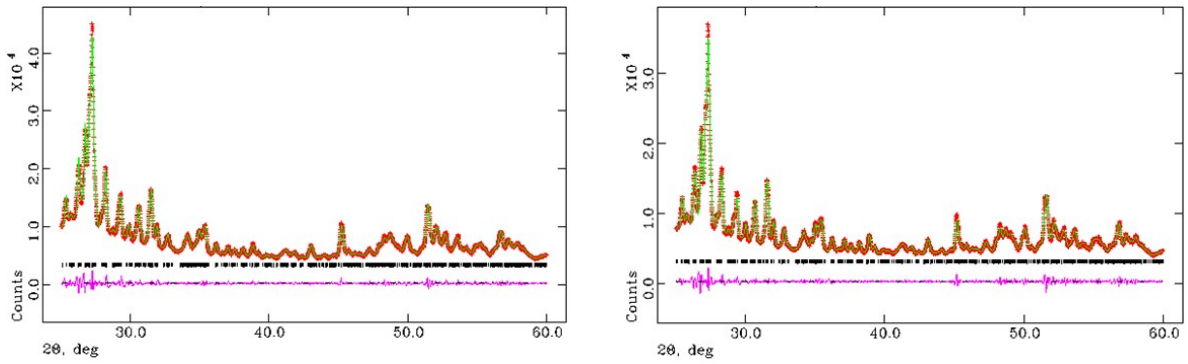


Fig. S7 PXRD patterns of $Li_xFe_2O_3$ prepared by the microwave-assisted chemical insertion: (a) x = 0.03, (b) x = 0.14, and (c) x = 0.15.

Scheme S1 Top: Structures of diethylene glycol (DEG) and tetraethylene glycol (TEG). Bottom: oxidation of ethylene glycol (EG) at 150 °C in air to glycolaldehyde (GA)[1,2]





(a) (b)

Fig. S8 Le Bail refinements of (a) the parent host compound $Mo_{2.48}VO_{9.93}$ and (b) Mg-inserted $Mg_xMo_{2.48}VO_{9.93}$ (x = 2) prepared by the microwave-assisted chemical insertion: *Pba*2, wR_p = 3.14%, lattice parameters a = 21.2675(2) Å, b = 26.7935(3) Å, and c = 4.1006(3) Å (measured, orange; calculated, green; difference, pink; Bragg reflections, vertical tick marks).

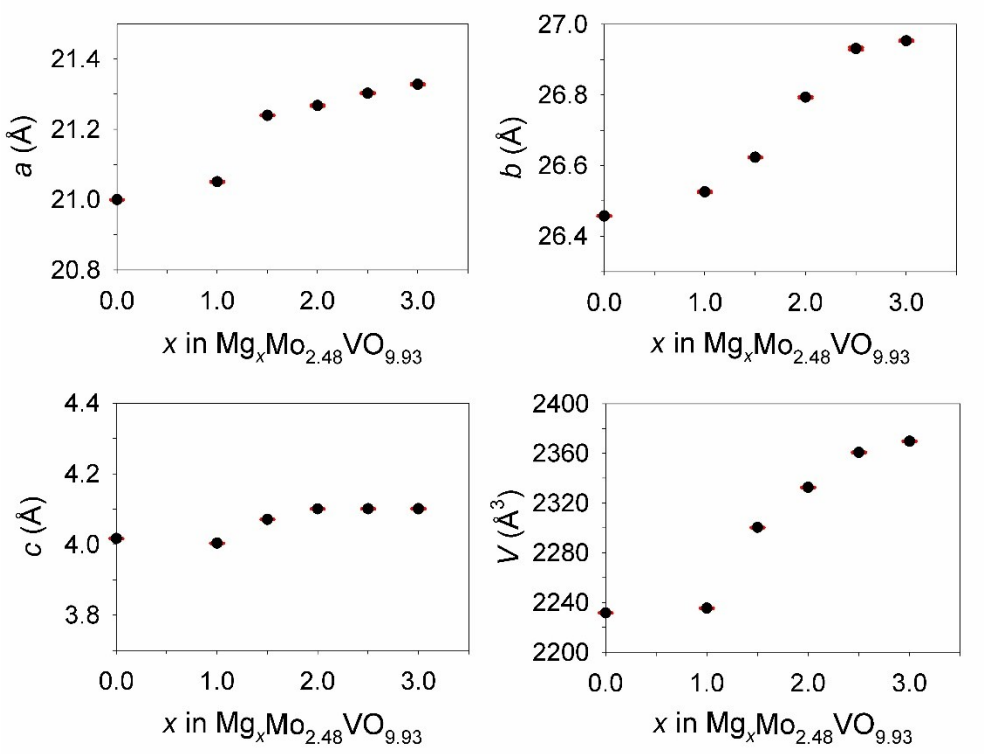


Fig. S9 Unit cell parameters of $Mg_xMo_{2.5+y}VO_{9+z}$ ($0 < x \leq 3$) prepared by the microwave-assisted chemical insertion with DEG and $Mg(CH_3COO)_2$, from Le Bail refinements (error bars in red).

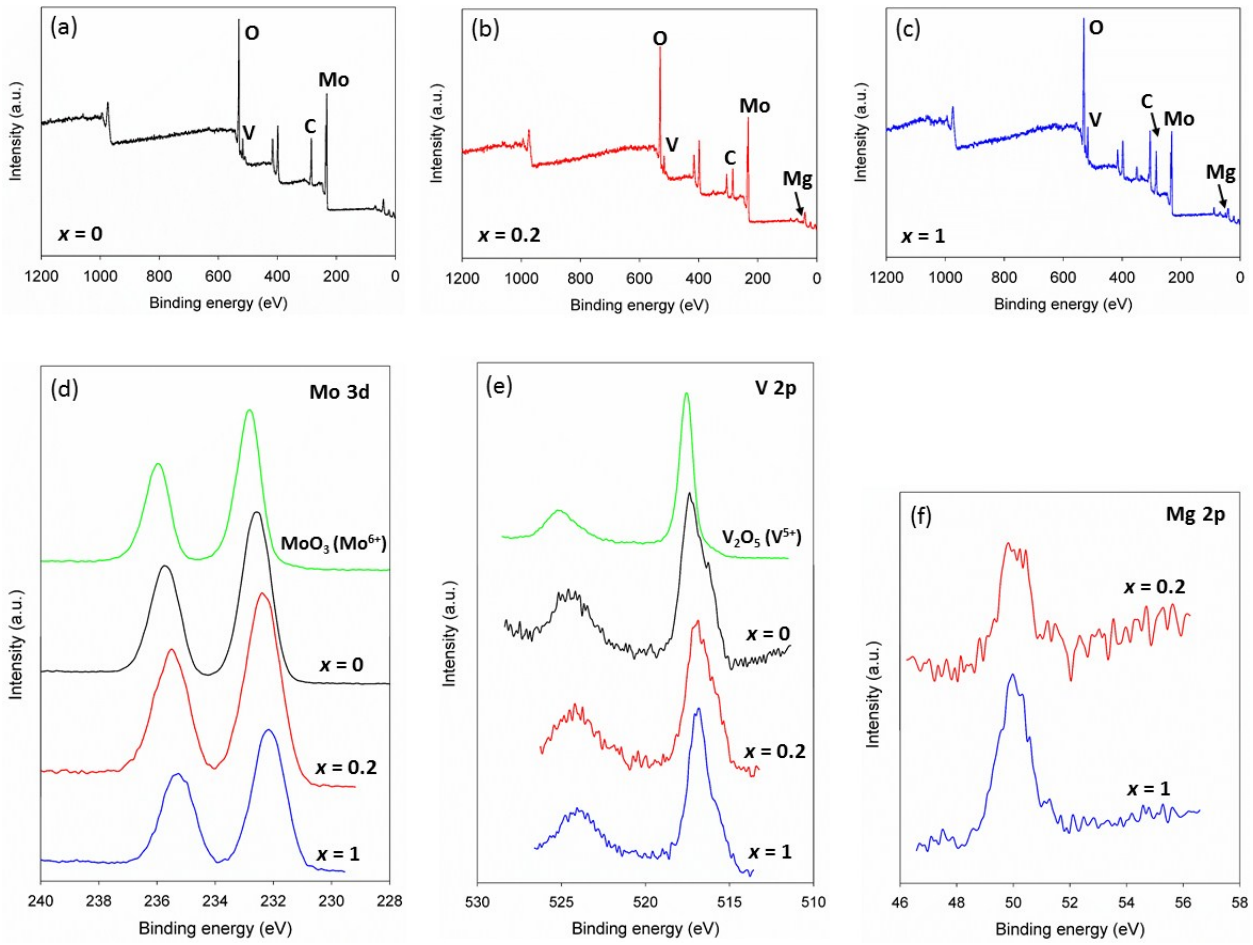


Fig. S10 X-ray photoelectron spectroscopy (XPS) data of $Mg_xMo_{2.5+y}VO_{9+z}$: (a, b, c) survey scans of $x = 0$, 0.2, and 1 samples. (d, e, f) high-resolution region scans of Mo 3d, V 2p, and Mg 2p using MoO_3 and V_2O_5 as reference compounds. The survey spectra reveal characteristic peaks of Mo, V, C, and O with Mg peaks only present in the Mg-inserted samples (b and c). High-resolution region spectra show a significant shift towards a lower binding energy in the Mg-inserted samples (x = 0.2 and 1) compared to the reference compounds MoO_3 (Mo^{6+} observed at 232.6 eV) and V_2O_5 (V^{5+} observed at 517.5 eV), suggesting the reduction of Mo and V ions. The characteristic peak of Mg 2p was observed at 50.0 eV in both the $x = 0.2$ and 1 samples, confirming the presence of Mg^{2+} in the Mg-inserted compounds.[3,4]

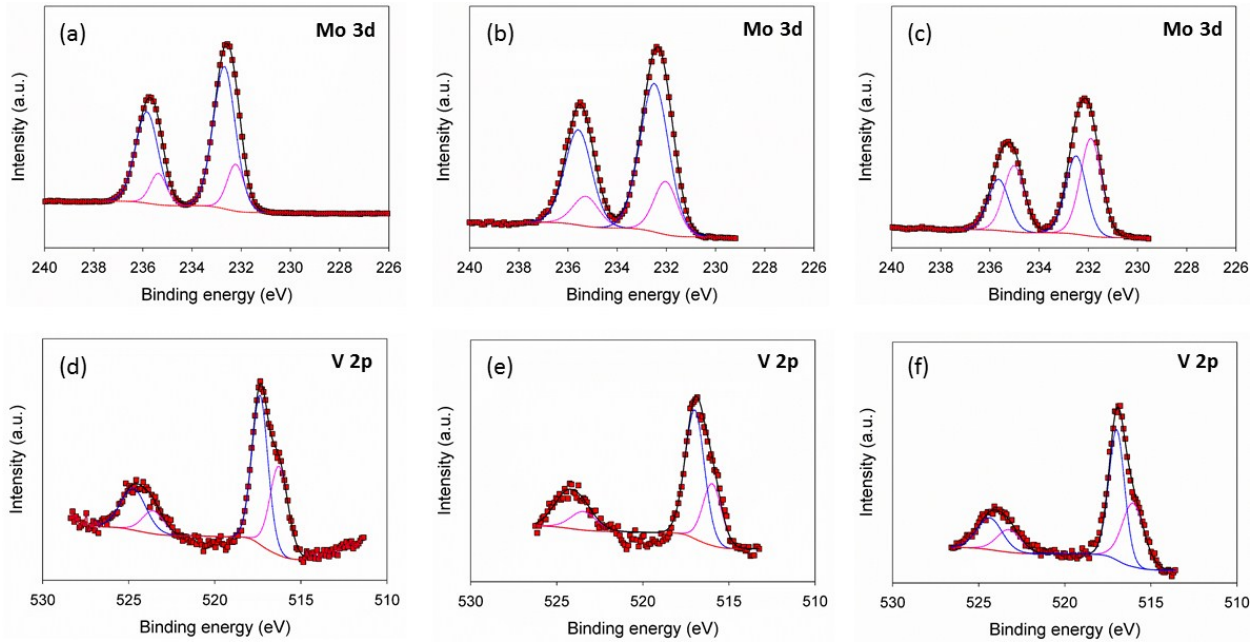


Fig. S11 Deconvolution of the $Mg_xMo_{2.5+y}VO_{9+z}$ high-resolution XPS spectra: (a, b, c) Mo $3d_{5/2}$ and $3d_{3/2}$ peaks of $x = 0$, 0.2, and 1, respectively (blue: Mo^{6+}, 232.6 eV; pink: Mo^{5+}, 232.0 eV). (d, e, f) V $2p_{3/2}$ and $2p_{1/2}$ peaks of $x = 0$, 0.2, and 1, respectively (blue: V^{5+}, 517.5 eV; pink: V^{4+}, 516.2 eV). The reduction of Mo and V ions takes place as the Mg 2p signal appears, thus confirming the Mg-insertion process.[5–8]

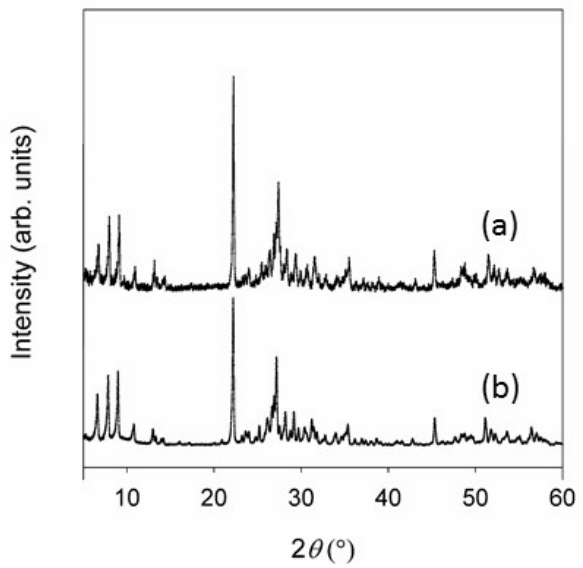


Fig. S12 X-ray diffraction pattern of $Mg_xMo_{2.5+y}VO_{9+z}$ electrode mixture (a) recovered from a cell at the end of first charge (after a complete removal of Mg^{2+}) compared to (b) that of a fresh Mg-inserted compound $Mg_xMo_{2.5+y}VO_{9+z}$ with $x = 1.6$, indicating that the host framework $Mo_{2.5+y}VO_{9+z}$ is maintained after the electrochemical extraction of Mg^{2+} ions.

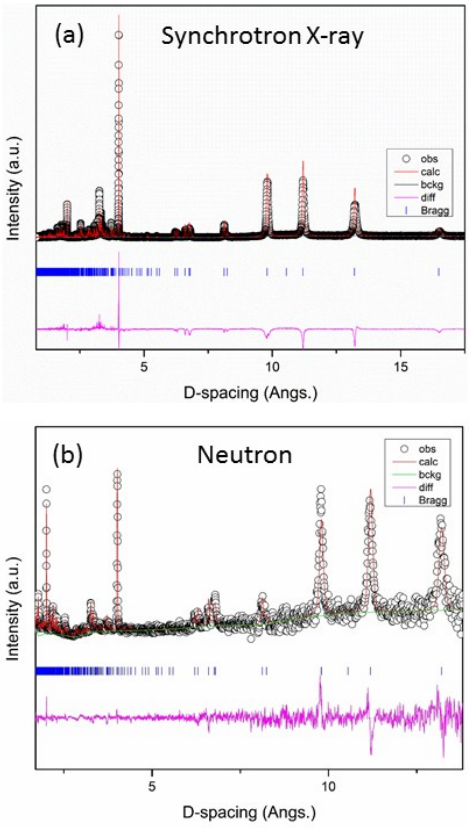


Fig. S13 (a) SXRD data and (b) NPD data (POWGEN Bank 5, wavelength 3.731 Å) from joint neutron and synchrotron X-ray Rietveld refinement of the parent host compound $Mo_{2.5+y}VO_{9+z}$.

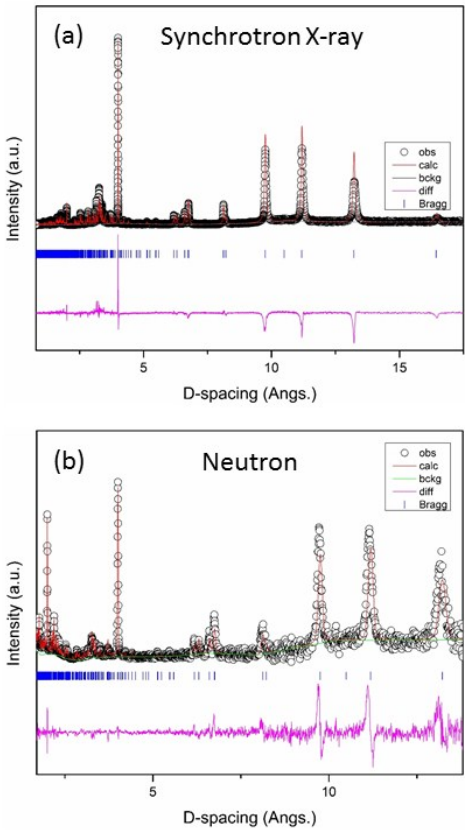


Fig. S14 (a) SXRD data and (b) NPD data (POWGEN Bank 5, wavelength 3.731 Å) from joint neutron and synchrotron X-ray Rietveld refinement of $Mg_xMo_{2.5+y}VO_{9+z}$ (x = 0.2).

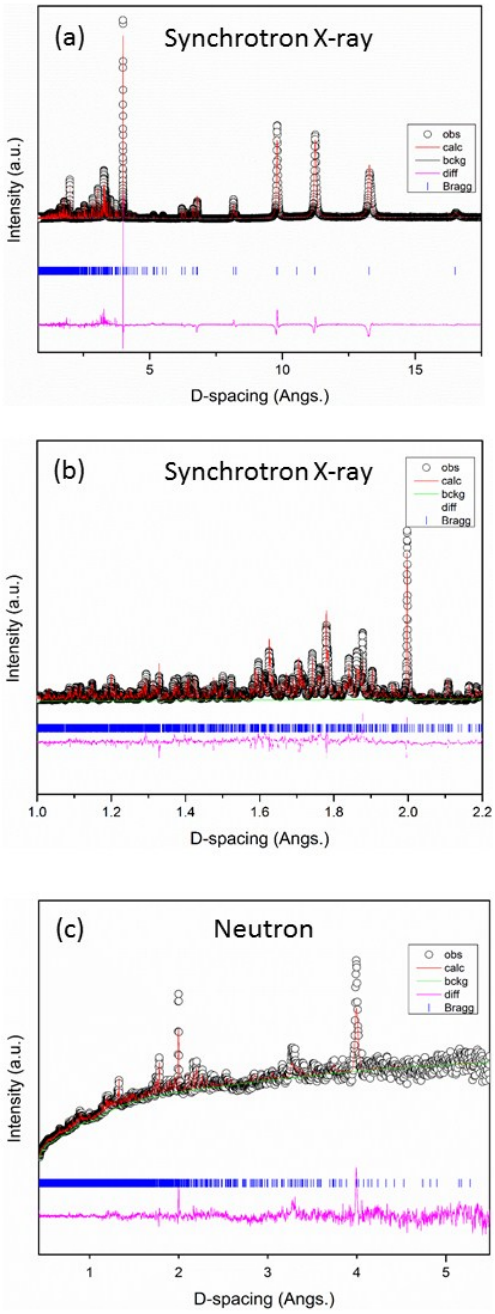


Fig. S15 Joint neutron and synchrotron X-ray Rietveld refinement of the Mg-inserted compound $Mg_xMo_{2.5+y}VO_{9+z}$, $x = 1$: (a) and (b) SXRD data. (c) NPD data from POWGEN Bank 3, wavelength 1.333 Å.

Table S2 Refined unit cell and atom site parameters of $Mo_{2.5+y}VO_{9+z}$ from combined neutron and synchrotron X-ray diffraction refinement

Unit Cell	*a* (Å)	*b* (Å)	*c* (Å)	*Z*	
*Pba*2	21.1040(4)	26.4037(3)	4.0133(0)	4	
Site	*x*	*y*	*z*	*U*iso *100	Frac. Occ.
Mo1	0	0	0.5085(29)	0.3	0.113
V1	0	0	0.5085(29)	0.3	0.887
Mo2	0	0.5	0.6502(21)	0.3	0.754
V2	0	0.5	0.6502(21)	0.3	0.246
Mo3	0.1206(4)	0.23764(29)	0.5363(20)	0.3	0.239
V3	0.1206(4)	0.23764(29)	0.5363(20)	0.3	0.761
Mo4	0.17529(30)	0.47811(22)	0.5382(18)	0.3	0.625
V4	0.17529(30)	0.47811(22)	0.5382(18)	0.3	0.375
Mo5	0.20947(23)	0.34449(17)	0.6822(18)	0.3	1
Mo6	0.27864(23)	0.21013(16)	0.6783(18)	0.3	1
Mo7	0.3819(4)	0.09999(26)	0.5507(22)	0.3	0.328
V7	0.3819(4)	0.09999(26)	0.5507(22)	0.3	0.672
Mo8	0.45966(22)	0.22309(17)	0.6855(17)	0.3	1
Mo9	0.36186(25)	0.31760(18)	0.55799	0.3	1
Mo10	0.00388(24)	0.13412(15)	0.6908(16)	0.3	1
Mo11	0.34417(25)	0.44217(17)	0.6688(17)	0.3	1
O1	0.0035(10)	0.0099(4)	0.114(4)	0.24	1
O2	0	0.5	0.128(6)	0.24	1
O3	0.1115(7)	0.2259(5)	0.105(4)	0.24	1
O4	0.1738(8)	0.4752(5)	0.112(5)	0.24	1
O5	0.2125(8)	0.3429(5)	0.090(5)	0.24	1
O6	0.2864(9)	0.2193(5)	0.125(5)	0.24	1
O7	0.3852(7)	0.1035(5)	0.103(5)	0.24	1
O8	0.4549(7)	0.2209(5)	0.101(5)	0.24	1
O9	0.3648(8)	0.3199(5)	0.128(4)	0.24	1
O10	-0.0030(8)	0.1378(5)	0.095(5)	0.24	1
O11	0.3409(8)	0.4326(5)	0.086(5)	0.24	1
O13	0.5350(8)	0.4304(6)	0.614(5)	0.24	1
O14	0.5773(8)	0.3333(5)	0.602(5)	0.24	1
O15	0.0400(9)	0.2717(5)	0.601(5)	0.24	1
O16	0.5798(8)	0.0320(5)	0.568(4)	0.24	1
O17	0.6949(9)	0.2980(5)	0.621(5)	0.24	1
O18	0.7788(8)	0.2188(6)	0.605(5)	0.24	1
O19	0.6714(8)	0.0957(5)	0.565(5)	0.24	1
O20	0.9642(8)	0.4323(5)	0.596(5)	0.24	1
O21	0.8047(9)	0.3531(5)	0.577(5)	0.24	1
O22	0.8027(8)	0.1238(5)	0.613(5)	0.24	1
O23	0.7693(7)	0.0250(6)	0.608(5)	0.24	1
O24	0.8667(9)	0.2551(5)	0.578(5)	0.24	1
O25	0.9084(9)	0.1220(6)	0.577(5)	0.24	1
O26	0.9042(8)	0.0147(5)	0.642(5)	0.24	1
O27	0.8283(7)	0.4536(5)	0.609(5)	0.24	1
O28	0.9382(8)	0.3416(5)	0.623(5)	0.24	1
O29	0.9516(8)	0.2022(5)	0.620(5)	0.24	1
O30	0.1537(9)	0.2961(6)	0.570(5)	0.24	1

Table S3 Refined unit cell and atom site parameters of $Mg_xMo_{2.5+y}VO_{9+z}$ ($x = 0.2$) from combined neutron and synchrotron X-ray refinement

Unit Cell	*a* (Å)	*b* (Å)	*c* (Å)	*Z*	
*Pba*2	20.9899(5)	26.4339(5)	4.0052(0)	4	
Site	*x*	*y*	*z*	*U*iso *100	Frac. Occ.
Mo1	0	0	0.5085	0.43	0.113
V1	0	0	0.5085	0.43	0.887
Mo2	0	0.5	0.6502	0.43	0.754
V2	0	0.5	0.6502	0.43	0.246
Mo3	0.1206	0.23764	0.5363	0.43	0.239
V3	0.1206	0.23764	0.5363	0.43	0.761
Mo4	0.17529	0.47811	0.5382	0.43	0.625
V4	0.17529	0.47811	0.5382	0.43	0.375
Mo5	0.20947	0.34449	0.6822	0.43	1
Mo6	0.27864	0.21013	0.6783	0.43	1
Mo7	0.3819	0.09999	0.5507	0.43	0.328
V7	0.3819	0.09999	0.5507	0.43	0.672
Mo8	0.45966	0.22309	0.6855	0.43	1
Mo9	0.36186	0.3176	0.55799	0.43	1
Mo10	0.00388	0.13412	0.6908	0.43	1
Mo11	0.34417	0.44217	0.6688	0.43	1
O1	0.0035	0.0099	0.114	0.13	1
O2	0	0.5	0.128	0.13	1
O3	0.1115	0.2259	0.105	0.13	1
O4	0.1738	0.4752	0.112	0.13	1
O5	0.2125	0.3429	0.09	0.13	1
O6	0.2864	0.2193	0.125	0.13	1
O7	0.3852	0.1035	0.103	0.13	1
O8	0.4549	0.2209	0.101	0.13	1
O9	0.3648	0.3199	0.128	0.13	1
O10	-0.003	0.1378	0.095	0.13	1
O11	0.3409	0.4326	0.086	0.13	1
O13	0.535	0.4304	0.614	0.13	1
O14	0.5773	0.3333	0.602	0.13	1
O15	0.04	0.2717	0.601	0.13	1
O16	0.5798	0.032	0.568	0.13	1
O17	0.6949	0.298	0.621	0.13	1
O18	0.7788	0.2188	0.605	0.13	1
O19	0.6714	0.0957	0.565	0.13	1
O20	0.9642	0.4323	0.596	0.13	1
O21	0.8047	0.3531	0.577	0.13	1
O22	0.8027	0.1238	0.613	0.13	1
O23	0.7693	0.025	0.608	0.13	1
O24	0.8667	0.2551	0.578	0.13	1
O25	0.9084	0.122	0.577	0.13	1
O26	0.9042	0.0147	0.642	0.13	1
O27	0.8283	0.4536	0.609	0.13	1
O28	0.9382	0.3416	0.623	0.13	1
O29	0.9516	0.2022	0.62	0.13	1
O30	0.1537	0.2961	0.57	0.13	1
Mg1	0.5256(13)	0.1295(13)	0.687(9)	0.25	0.32612
Mg2	0.7120(13)	0.3722(9)	0.691(9)	0.25	0.33807

Table S4 Refined unit cell and atom site parameters of $Mg_xMo_{2.5+y}VO_{9+z}$ (x = 1) from combined neutron and synchrotron X-ray refinement

Unit Cell	*a* (Å)	*b* (Å)	*c* (Å)	*Z*	
*Pba*2	21.0882(1)	26.5344(2)	3.9946(0)	4	
Site	*x*	*y*	*z*	*U*iso *100	Frac. Occ.
Mo1	0	0	0.5085	0.65	0.113
V1	0	0	0.5085	0.65	0.887
Mo2	0	0.5	0.6502	0.65	0.754
V2	0	0.5	0.6502	0.65	0.246
Mo3	0.1206	0.23764	0.5363	0.65	0.239
V3	0.1206	0.23764	0.5363	0.65	0.761
Mo4	0.17529	0.47811	0.5382	0.65	0.625
V4	0.17529	0.47811	0.5382	0.65	0.375
Mo5	0.20947	0.34449	0.6822	0.65	1
Mo6	0.27864	0.21013	0.6783	0.65	1
Mo7	0.3819	0.09999	0.5507	0.65	0.328
V7	0.3819	0.09999	0.5507	0.65	0.672
Mo8	0.45966	0.22309	0.6855	0.65	1
Mo9	0.36186	0.3176	0.55799	0.65	1
Mo10	0.00388	0.13412	0.6908	0.65	1
Mo11	0.34417	0.44217	0.6688	0.65	1
O1	0.0035	0.0099	0.114	0.38	1
O2	0	0.5	0.128	0.38	1
O3	0.1115	0.2259	0.105	0.38	1
O4	0.1738	0.4752	0.112	0.38	1
O5	0.2125	0.3429	0.09	0.38	1
O6	0.2864	0.2193	0.125	0.38	1
O7	0.3852	0.1035	0.103	0.38	1
O8	0.4549	0.2209	0.101	0.38	1
O9	0.3648	0.3199	0.128	0.38	1
O10	-0.003	0.1378	0.095	0.38	1
O11	0.3409	0.4326	0.086	0.38	1
O13	0.535	0.4304	0.614	0.38	1
O14	0.5773	0.3333	0.602	0.38	1
O15	0.04	0.2717	0.601	0.38	1
O16	0.5798	0.032	0.568	0.38	1
O17	0.6949	0.298	0.621	0.38	1
O18	0.7788	0.2188	0.605	0.38	1
O19	0.6714	0.0957	0.565	0.38	1
O20	0.9642	0.4323	0.596	0.38	1
O21	0.8047	0.3531	0.577	0.38	1
O22	0.8027	0.1238	0.613	0.38	1
O23	0.7693	0.025	0.608	0.38	1
O24	0.8667	0.2551	0.578	0.38	1
O25	0.9084	0.122	0.577	0.38	1
O26	0.9042	0.0147	0.642	0.38	1
O27	0.8283	0.4536	0.609	0.38	1
O28	0.9382	0.3416	0.623	0.38	1
O29	0.9516	0.2022	0.62	0.38	1
O30	0.1537	0.2961	0.57	0.38	1
Mg1	0.5256	0.1295	0.687	0.3(5)	0.5202
Mg2	0.712	0.3722	0.691	0.3(9)	0.30103

References

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