Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary information

Table S1: Formation energies calculated in meV/formula unit for the different structural hypothesis for VPO_4O with GGA and GGA + U versus the most stable phase (the one described in Cc).

VPO_4O	GGA	GGA + U			
		U = 3 eV	U = 4 eV	U = 4.5 eV	
Cc	0	0	0	0	most stable
$P2_1/n$	7	7	7	8	
P-1	33	28	27	27	
C2/c	420	361	343	334	

Table S2: Cell parameters and V-O bonds distances resulting from the structural optimization using GGA + U (U = 4eV) with the VASP code.

GGA+U (U = 4eV)	VPO_4O	Cc	$P2_1/n$	P-1	C2/c
	a (Å)	7.326	7.311	6.962	7.221
	b (Å)	7.07	7.135	7.705	7.304
	c (Å)	7.371	7.408	7.598	7.24
	α (°)	90	90	90.78	90
	β (°)	115.19	115.02	90.23	121.54
	γ (°)	90	90	119.61	90
	d_{V-O} (Å)				
	V(1)-O	1.609	1.609	1.612	1.819 x2
		1.884	1.887	1.892	1.903 x2
		1.917	1.905	1.895	1.929 x2
		1.919	1.909	1.912	
		1.919	1.917	1.922	
		2.574	2.585	2.524	
	V(2)-O	-	-	1.611	-
				1.891	
				1.909	
				1.914	
				1.925	
				2.497	

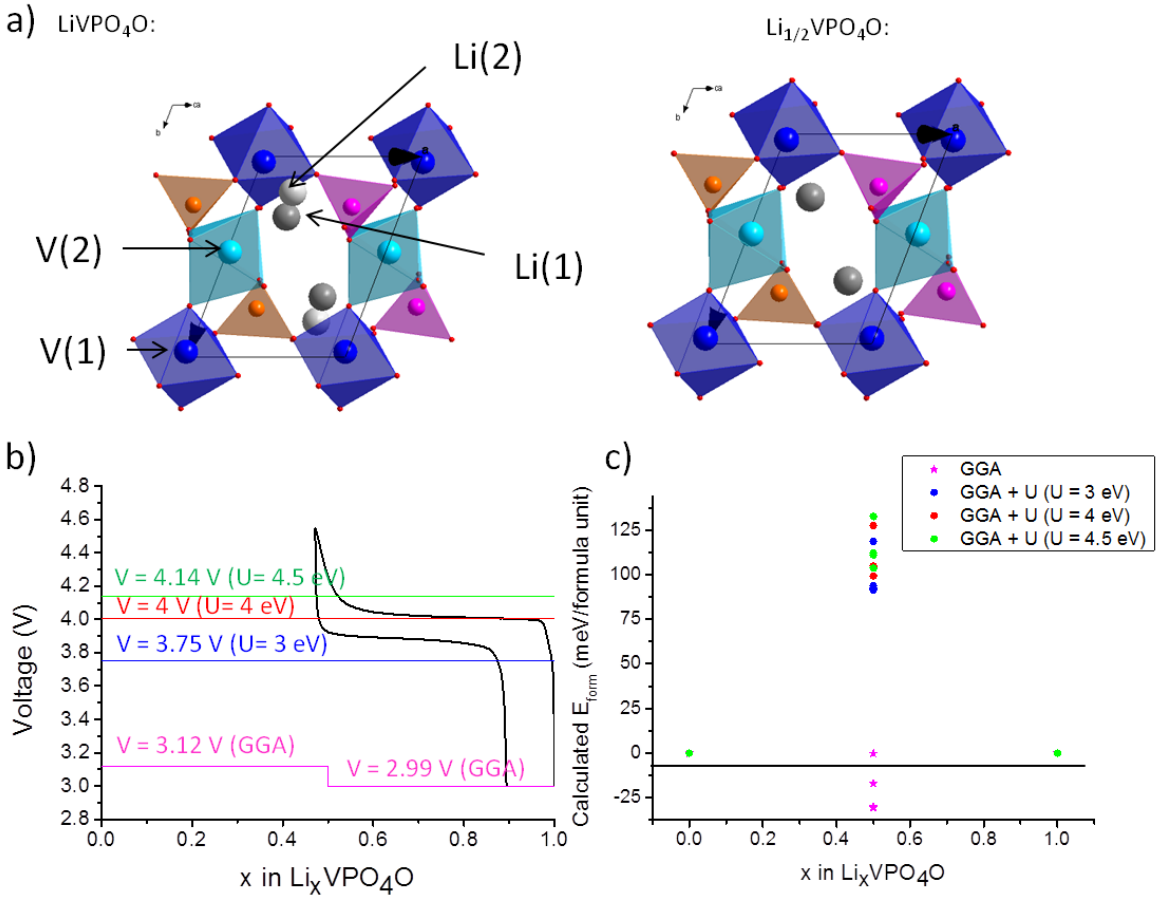

Figure S1: a) Crystal structure before relaxation used for DFT calculations. $LiVPO_4O$ from published experimental data (left) and $Li_{0.5}VPO_4O$ (right). $Li_{0.5}VPO_4O$ is obtained from $LiVPO_4O$ with different occupations of the Li1 and Li2 sites. The most stable structure is the one with the site Li1 only occupied. b) Various values of U used for GGA+U calculations applied on the 3d orbitals of V ions and resulting potentials. U = 4eV represents the best choice. c) Formation energy for $Li_{0.5}VPO_4O$ for different U values. The phase would be stable with respect to $LiVPO_4O$ and VPO_4O only for U = 0.

Table S3: Refined parameters for VPO_4O. Comparison between Cc and $P2_1/n$ space groups.

VPO_4O	**Cc**	**$P2_1/n$**
χ^2, R_{Bragg}, R_{wp}	2.83, 3.9%, 12.3%	3.57, 6.77%, 14.8%
a, b, c, (Å) γ (°), Vol (Å^3)	7.2699(6), 6.8773(4), 7.2598(5), 115.382(2), 327.93(4)	7.2684(6), 6.8772(4), 7.2605(6), 115.384(3), 327.89(4)
V–O distances (Å) / distortion	1.85(2), 1.86(3), 1.86(2), 1.93(2), 1.59(2), 2.51(2) 41.95 * 10^{-4}	1.83(3), 1.82(2), 1.88(1), 1.95(3), 1.58(2), 2.52(2) 48.07 * 10^{-4}
P-O distances (Å) / distortion	1.55(2), 1.56(3), 1.55(3), 1.48(2) 4.98 *10^{-4}	1.52(2), 1.63(3), 1.50(3), 1.60(2) 12.36 *10^{-4}

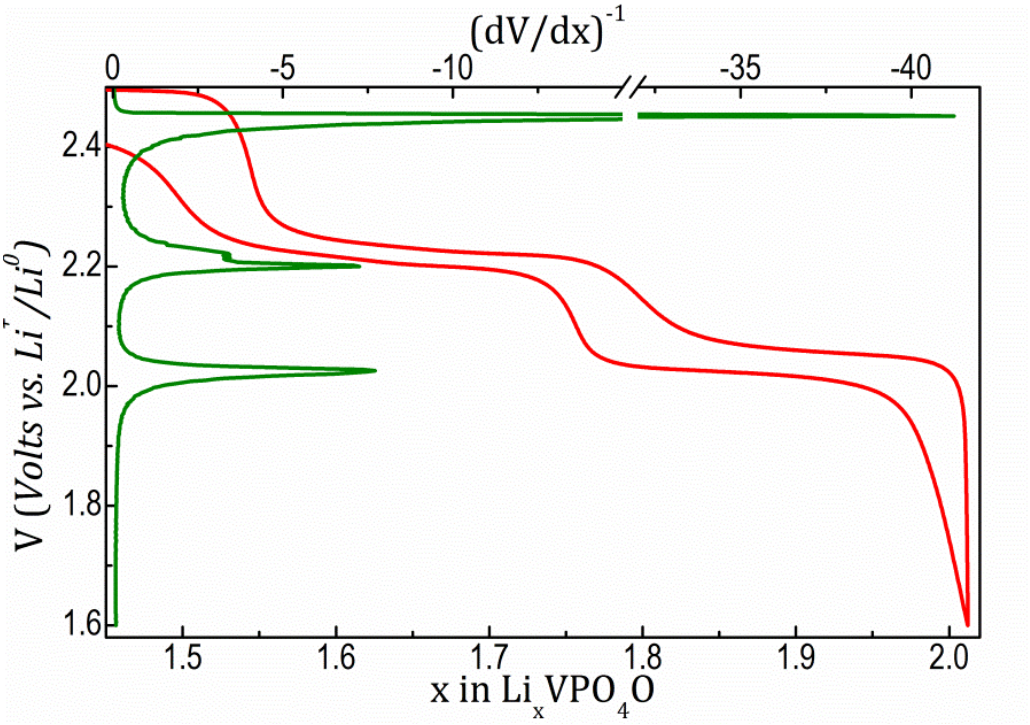

Figure S2: Galvanostatic cycling for a mixture of 80 wt% $LiVPO_4O$ and 20 wt% Csp (SPEX ball-milled for 30 minutes). Focus on the low voltage region between compositions $Li_{1.5}VPO_4O$ and Li_2VPO_4O.