

ARTICLE

Electronic Supplementary Information

Table S1. Calculated dopant formation energies shown in Fig. 8.

E_f (eV/dopant)	3.125%	6.25%	9.375%	12.5%
Nb (β)	1.06	0.79	0.70	0.63
Nb (ε)	0.40	0.29	0.25	0.18
Ti (β)	0.43	0.20	0.13	0.0074
Ti (ε)	0.105	0.056	0.039	-0.023

Table S2. ICP data of Ti- and Nb-substituted $\text{LiVOPO}_4 \cdot 2\text{H}_2\text{O}$, relative to P.

% Subs from synthesis	Ti				Nb			
	Li	V	P	Ti	Li	V	P	Nb
0	1.031	1.003	1.000					
1	0.971	0.965	1.000	0.012	0.964	1.006	1.000	0.008
2.5	1.023	1.011	1.000	0.031	0.927	0.990	1.000	0.027
5	0.981	0.962	1.000	0.062	0.935	0.951	1.000	0.077
10	0.875	0.871	1.000	0.136	0.750	0.910	1.000	0.149
15					0.445	0.774	1.000	0.270
20					0.333	0.648	1.000	0.386

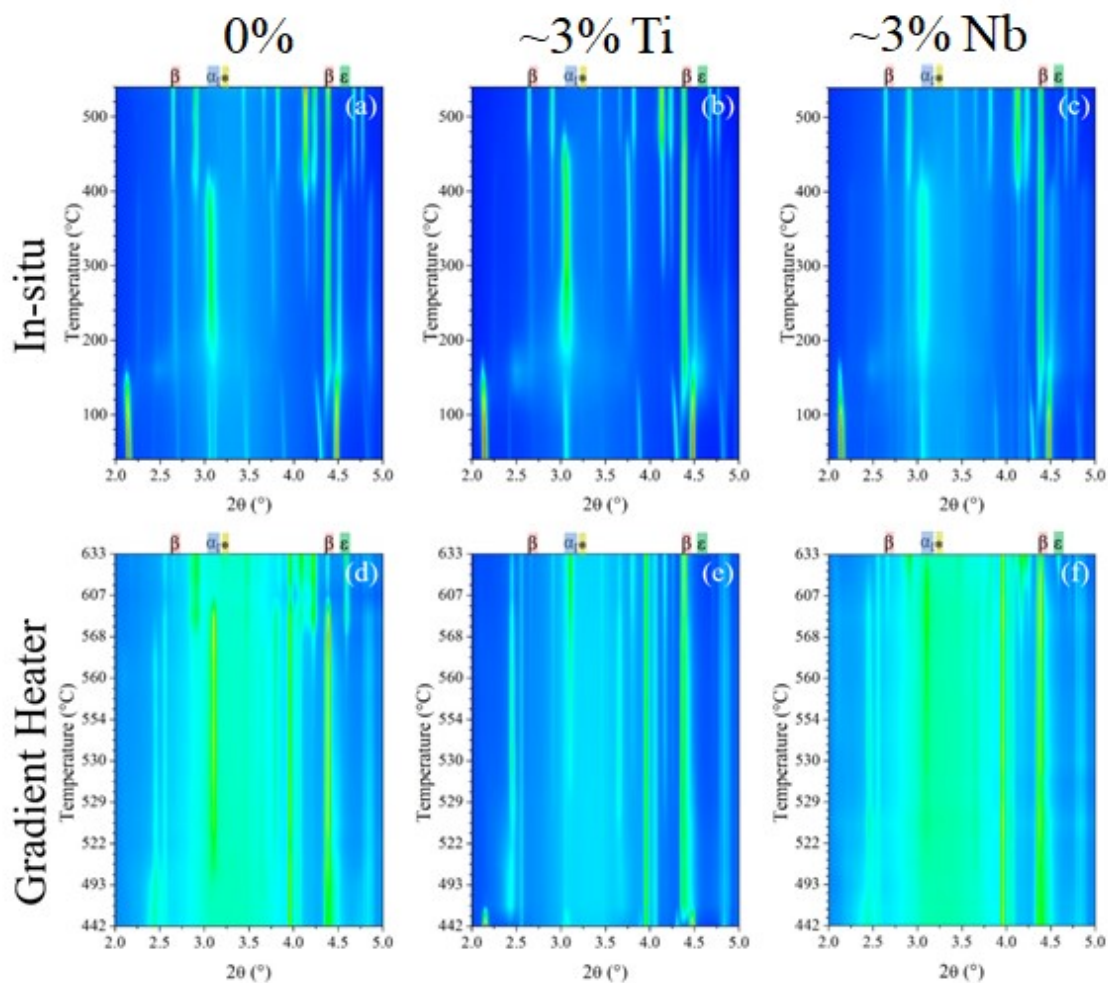


Fig. S1. Comparison of XRD while heating pristine and substituted $\text{LiVOPO}_4 \cdot 2\text{H}_2\text{O}$ in O_2 via (a-c) the in-situ method or (d-f) the gradient heater method.

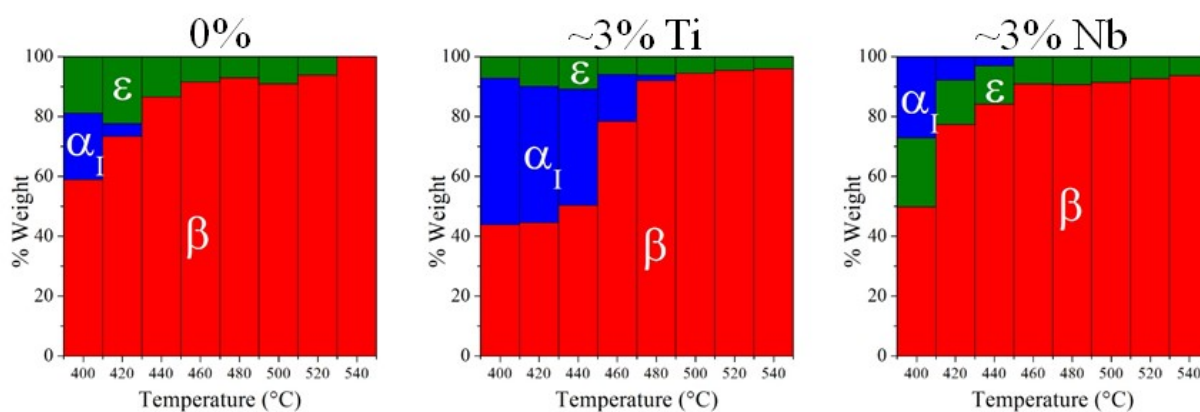
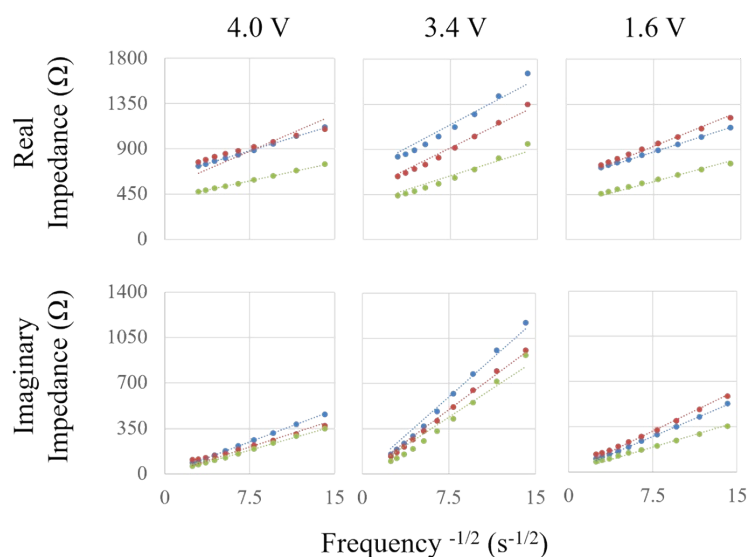


Fig. S2. Phase quantification from in-situ heating in O_2 with XRD comparing pristine and substituted $\text{LiVOPO}_4 \cdot 2\text{H}_2\text{O}$.

Table S3. Values for α from EIS fittings of the Warburg impedance using a CPE.

Sample	α (ideal value is 0.5)			Angle (ideal value is 45 °)		
	Pristine	1% Nb	3% Ti	Pristine	1% Nb	3% Ti
4.0 V	0.501	0.249	0.509	45.09	22.41	45.81
3.4 V	0.6136	0.551	0.653	55.224	49.59	58.77
1.6 V	0.501	0.431	0.432	45.09	38.826	38.853

Fig. S3. Plots of frequency^{-1/2} vs either the real or imaginary impedance of the linear, low-frequency regions of the EIS for calculating the Warburg coefficients for the (blue) pristine, (red) 1% Nb-substituted, and (green) 3% Ti-substituted β -LiVOPO₄.Table S4. Linear fitting values for the plots in Fig. S3; m is the slope, b is the y-intercept, and R² is the linear regression goodness of fit. The slopes are equal to the Warburg coefficients of those samples.

Impedance	Subs	4.0 V			3.4 V			1.6 V		
		m	b	R ²	m	b	R ²	m	b	R ²
Real	Pris	34.3	623.0	0.998	61.3	685.3	0.952	37.1	597.6	0.997
	1% Nb				56.8	488.1	0.980	46.9	578.3	0.981
	3% Ti	24.1	401.5	0.998	36.6	363.3	0.937	31.1	346.5	0.971
Imaginary	Pris	32.8		0.999	79.3		0.985	36.9		0.998
	1% Nb				66.4		0.993	42.1		0.990
	3% Ti	24.6		0.999	58.5		0.958	25.7		0.988

Table S5. Slopes of the (dis)charge profile right before conducting EIS measurements

Voltage (V)	Slope of (dis)charge profile		
	Pristine	1% Nb	3% Ti
4.0	1.59		1.55
3.4	-4.11	-3.89	-4.78
1.6	-1.24	-0.88	-1.16

Calculation of the bulk Li⁺ diffusion coefficient (D_W) is then calculated using the following equation proposed by Ho *et al.*¹

$$D_W = \frac{1}{2} \left(\frac{V_M}{zFa\sigma} \right)^2 \left(\frac{dE}{dx} \right)^2$$

where D_W is the bulk Li⁺ diffusion coefficient, V_M is the molar volume of β -LiVOPO₄ (50.61 cm³/mol), z is the number of electrons transferred during the reaction (1 e⁻), F is Faraday's constant, a is the electrode surface area (1.2 cm²), σ is the Warburg coefficient (Table S4), and dE/dx is the slope of the cycling profile (x in Li _{x} VOPO₄ vs V) right before taking EIS measurements (Table S5).

References in ESI

1. C. Ho, I. D. Raistrick and R. A. Huggins, *Journal of The Electrochemical Society*, 1980, **127**, 343.