Supplementary Information

Electronic Structure, Ion Diffusion and Cation Doping in the $Na_4VO(PO_4)_2$ Compound as a Cathode Material for Na-ion Batteries

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Table SI1. Pedone interatomic potential parameters of $NaVOPO_4$ polymorphs.[1] The V-O parameters were optimized using the GULP software.[2]

Buckingham: $Ae^{-r/\rho} - Cr^{-6}$	**A (eV)**	**ρ (Å)**	**C (eV Å^6)**	**Cut-off (Å)**
$Na^{0.6}$-$O^{-1.2}$	2010.33	0.261901	28.1687	r_{min} = 0.0/r_{max} = 15.0
P^{3}-$O^{-1.2}$	28357	0.178335	68.0998	r_{min} = 0.0/r_{max} = 15.0
V^{3}-$O^{-1.2}$	2306.19	0.228157	0	r_{min} = 0.0/r_{max} = 15.0
$V^{2.4}$-$O^{-1.2}$	2306.19	0.228157	0	r_{min} = 0.0/r_{max} = 15.0
$O^{-1.2}$-$O^{-1.2}$	2067.72	0.342846	214.2	r_{min} = 0.0/r_{max} = 15.0

Table SI2. Computed and experimental bond lengths of β-$Na_4VO(PO_4)_2$ compound (in Å).

	β-$Na_4VO(PO_4)_2$	
	Comp.	Exp.[a]
V-O	1.749	1.845
	1.940	1.868
	1.966	1.945
	1.977	1.950
	1.989	1.967
	2.043	1.992
P-O	1.527	1.518
	1.542	1.519
	1.561	1.529
	1.564	1.615
Na(1)-O	2.297	2.260
	2.324	2.336
	2.394	2.431
	2.432	2.452
	2.433	2.478
	2.459	2.507
Na(2)-O	2.243	2.223
	2.247	2.234
	2.312	2.285
	2.329	2.414
	2.712	2.657
	2.816	2.853
Na(3)-O	2.271	2.309
	2.332	2.323
	2.372	2.369
	2.410	2.492
Na(4)-O	2.325	2.301
	2.460	2.489
	2.470	2.536
	2.517	2.600
	2.617	2.623
	2.624	2.698
	2.823	2.756

[a] Ref. [3].

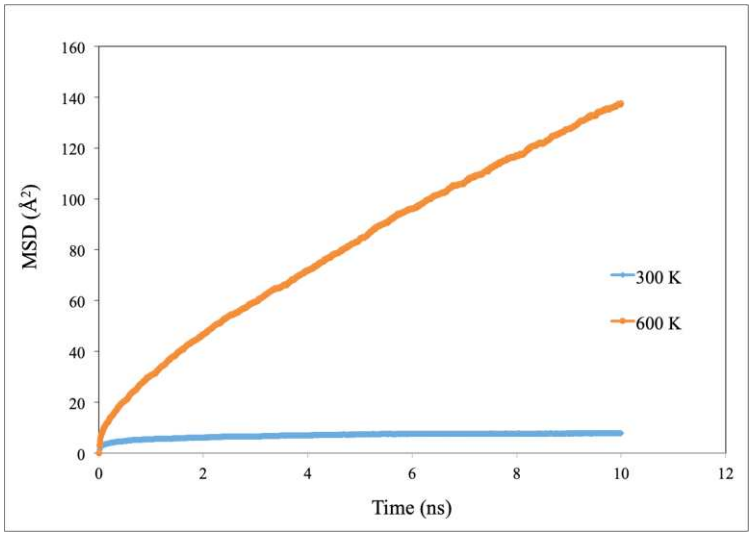

Figure SI1. Mean square displacement (MSD) *vs.* time for the $Na_4VO(PO_4)_2$ compound at 300 and 600 K.

References

1 A. Pedone, G. Malavasi, M. C. Menziani, A. N. Cormack and U. Segre, *J. Phys. Chem. B*, 2006, **110**, 11780–11795.

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