Supplementary Information

Efficient proton conductivity in a novel 3D open-framework vanadoborate with $[V_6B_{20}]$ architectures

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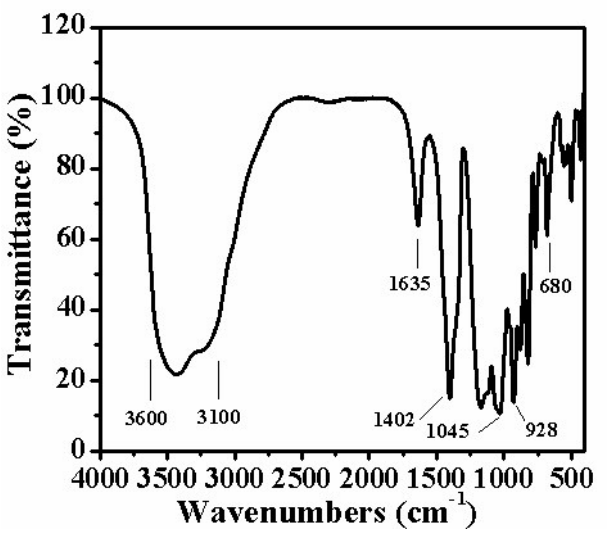


Fig. S1 FT-IR spectrum of compound **1**.

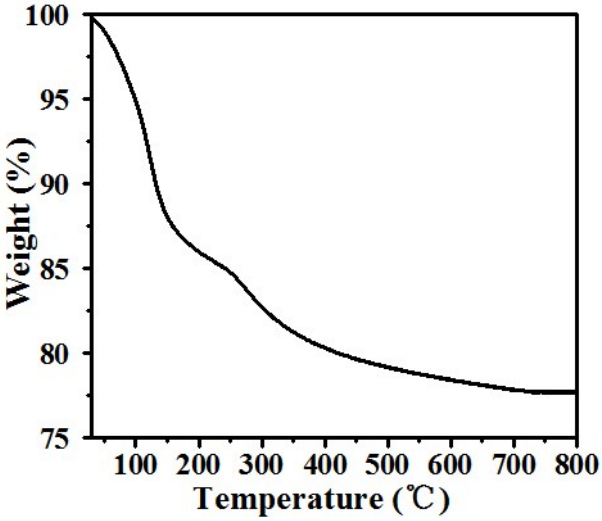
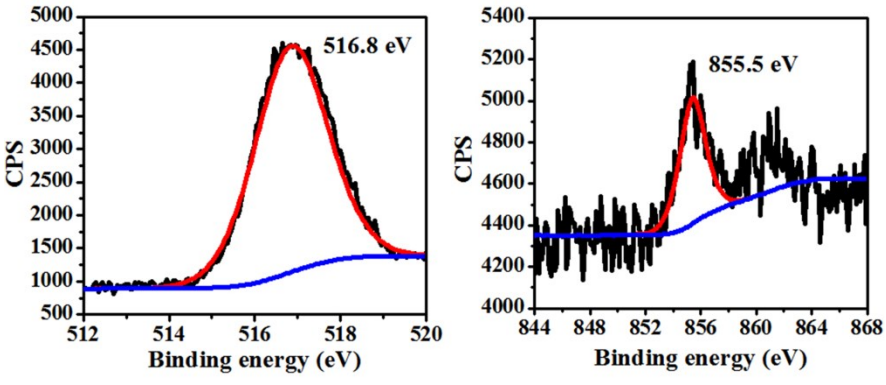


Fig. S2 TGA curve of compound **1**.



(a) (b)

Fig. S3 XPS spectra of V $^2P_{3/2}$ (a) and Ni $^2P_{3/2}$ (b).

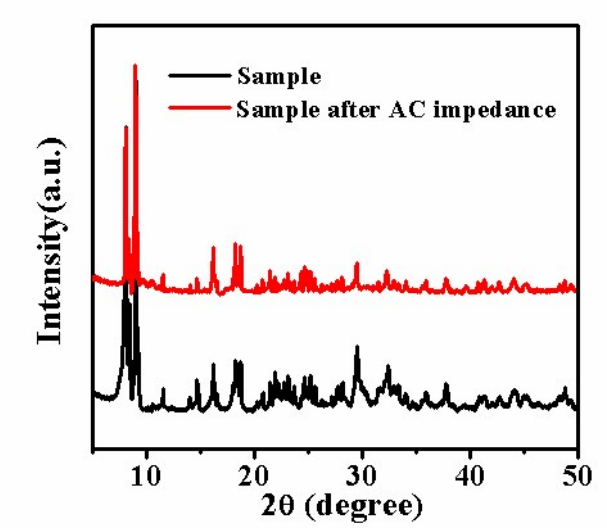


Fig. S4 The XRD patterns of sample (black) and the sample used impedance measurement.

Table S1 Selected bonds length (Å) and angles (°) for **1**.

Ni(1)-O(8)	2.024(4)	V(1)-O(23)	1.601(5)
Ni(1)-O(8)#1	2.024(4)	V(1)-O(17)	1.959(4)
Ni(1)-O(26)	2.069(5)	V(1)-O(19)	1.960(4)
Ni(1)-O(26)#1	2.068(5)	V(1)-O(11)#2	1.972(4)
Ni(1)-O(12)	2.075(4)	V(1)-O(9)#2	1.976(4)
Ni(1)-O(12)#1	2.076(4)	V(3)-O(25)	1.612(5)
V(2)-O(24)	1.616(5)	V(3)-O(6)#2	1.950(4)
V(2)-O(17)	1.946(4)	V(3)-O(15)	1.951(4)
V(2)-O(6)#2	1.948(5)	V(3)-O(11)	1.955(4)
V(2)-O(15)	1.965(4)	V(3)-O(19)#2	1.960(4)
V(2)-O(9)#2	1.971(4)	B(1)-O(1)	1.475(8)
B(2)-O(5)	1.420(8)	B(1)-O(2)	1.423(8)
B(2)-O(6)	1.461(8)	B(1)-O(3)	1.530(8)
B(2)-O(7)	1.470(8)	B(1)-O(4)	1.467(8)
B(2)-O(1)	1.530(8)	B(3)-O(1)	1.523(8)
B(4)-O(3)	1.503(8)	B(3)-O(8)	1.436(8)
B(4)-O(8)	1.439(8)	B(3)-O(9)	1.454(8)
B(4)-O(11)	1.437(8)	B(3)-O(10)	1.452(8)
B(4)-O(12)	1.488(8)	B(5)-O(3)	1.541(8)
B(6)-O(2)	1.539(8)	B(5)-O(13)	1.469(8)

B(6)-O(14)	1.426(8)	B(5)-O(14)	1.421(8)
B(6)-O(16)	1.462(8)	B(5)-O(15)	1.461(8)
B(6)-O(17)	1.465(8)	B(7)-O(5)	1.416(8)
B(8)-O(7)	1.358(8)	B(7)-O(2)	1.539(8)
B(8)-O(10)	1.369(7)	B(7)-O(18)	1.473(8)
B(8)-O(20)	1.371(8)	B(7)-O(19)	1.446(8)
B(10)-O(16)	1.367(9)	B(9)-O(12)	1.374(8)
B(10)-O(18)	1.473(8)	B(9)-O(13)	1.364(8)
B(10)-O(22)	1.382(9)	B(9)-O(21)	1.363(8)
Na(1)-O(5)	2.246(6)	O(23)-V(1)-O(17)	109.7(2)
Na(1)-O(7)	2.584 (6)	O(23)-V(1)-O(19)	108.3(2)
Na(1)-O(27)	2.404(10)	O(17)-V(1)-O(19)	91.00(18)
Na(1)-O(28A)	2.726(17)	O(23)-V(1)-O(11)#2	109.6(2)
Na(1)#4-O(20)	2.292(7)	O(17)-V(1)-O(11)#2	140.66(18)
Na(1)#5-O(22)	2.267(14)	O(19)-V(1)-O(11)#2	75.77(18)
Na(2)-O(14)	2.424(9)	O(23)-V(1)-O(9)#2	110.1(2)
Na(2)-O(4)	2.627(9)	O(17)-V(1)-O(9)#2	76.85(17)
Na(2)-O(30A)	2.562(6)	O(19)-V(1)-O(9)#2	141.59(19)
Na(2)-O(30B)	2.462(2)	O(11)#2-V(1)-O(9)#2	90.75(18)
Na(2)-O(29A)	2.511(16)	O(24)-V(2)-O(17)	110.4(2)
Na(2)#3-O(14)	2.402(9)	O(24)-V(2)-O(6)#2	109.7(2)
O(25)-V(3)-O(6)#2	109.9(2)	O(17)-V(2)-O(6)#2	139.85(18)
O(25)-V(3)-O(15)	109.5 (2)	O(24)-V(2)-O(15)	110.5(2)
O(6)#2-V(3)-O(15)	77.00(18)	O(17)-V(2)-O(15)	89.48(18)
O(25)-V(3)-O(11)	109.0(2)	O(6)#2-V(2)-O(15)	76.70(18)
O(6)#2-V(3)-O(11)	141.11(19)	O(24)-V(2)-O(9)#2	108.6(2)
O(15)-V(3)-O(11)	90.48(18)	O(17)-V(2)-O(9)#2	77.27(17)
O(25)-V(3)-O(19)#2	109.4(2)	O(6)#2-V(2)-O(9)#2	89.98(18)
O(6)#2-V(3)-O(19)#2	90.68(18)	O(15)-V(2)-O(9)#2	140.88(18)
O(15)-V(3)-O(19)#2	141.06(18)	O(4)-B(1)-O(2)	112.1(5)
O(11)-V(3)-O(19)#2	76.17(18)	O(4)-B(1)-O(1)	111.8(5)
O(5)-B(2)-O(6)	113.4(5)	O(2)-B(1)-O(1)	109.1(5)
O(5)-B(2)-O(7)	110.3(5)	O(4)-B(1)-O(3)	109.3(5)
O(6)-B(2)-O(7)	109.5(5)	O(2)-B(1)-O(3)	106.7(5)
O(5)-B(2)-O(1)	108.6(5)	O(1)-B(1)-O(3)	107.5(5)
O(6)-B(2)-O(1)	107.7(5)	O(8)-B(3)-O(10)	110.9(5)
O(7)-B(2)-O(1)	107.2(5)	O(8)-B(3)-O(9)	110.7(5)
O(11)-B(4)-O(8)	113.9(5)	O(10)-B(3)-O(9)	111.7(5)
O(11)-B(4)-O(12)	112.0(5)	O(8)-B(3)-O(1)	108.0(5)
O(8)-B(4)-O(12)	104.0(5)	O(10)-B(3)-O(1)	107.8(5)

O(11)-B(4)-O(3)	109.6(5)	O(9)-B(3)-O(1)	107.7(5)
O(8)-B(4)-O(3)	109.4(5)	O(14)-B(5)-O(15)	113.3(5)
O(12)-B(4)-O(3)	107.6(5)	O(14)-B(5)-O(13)	111.0(5)
O(14)-B(6)-O(16)	110.4(5)	O(15)-B(5)-O(13)	110.8(5)
O(14)-B(6)-O(17)	113.2(5)	O(14)-B(5)-O(3)	108.1(5)
O(16)-B(6)-O(17)	110.2(5)	O(15)-B(5)-O(3)	106.8(5)
O(14)-B(6)-O(2)	109.1(5)	O(14)-B(5)-O(3)	106.5(5)
O(16)-B(6)-O(2)	107.1(5)	O(5)-B(7)-O(19)	113.8(5)
O(17)-B(6)-O(2)	106.6(5)	O(5)-B(7)-O(18)	110.5(5)
O(7)-B(8)-O(20)	121.3(6)	O(19)-B(7)-O(18)	109.8(5)
O(7)-B(8)-O(10)	123.1(6)	O(5)-B(7)-O(2)	108.7(5)
O(20)-B(8)-O(10)	115.5(6)	O(19)-B(7)-O(2)	107.2(5)
O(18)-B(10)-O(16)	124.3(6)	O(18)-B(7)-O(2)	106.5(5)
O(18)-B(10)-O(22)	116.3(6)	O(21)-B(9)-O(13)	118.2(6)
		O(21)-B(9)-O(12)	119.8(6)
		O(12)-B(9)-O(13)	122.0(6)
		O(16)-B(10)-O(22)	119.4(6)

Symmetry transformations used to generate equivalent atoms:
#1 –x+2,-y+1,-z+2 #2 -x+1,-y+1,-z+2 #3 x+1,-y+1/2,-z+1
#4 x+1/2,-y+1/2,z+1/2 #5 x-1/2,-y-1/2,z-1/2

Table S2 The BVS calculations suggest the following central atom valencies :

Ni1	+2	(0.146)	B5	+3	(0.057)
V1	+4	(0.078)	B6	+3	(0.055)
V2	+4	(0.078)	B7	+3	(0.098)
V3	+4	(0.121)	B8	+3	(0.018)
B1	+3	(0.047)	B9	+3	(0.038)
B2	+3	(0.078)	B10	+3	(0.020)
B3	+3	(0.106)	Na1	+1	(0.034)
B4	+3	(0.096)	Na2	+1	(0.052)