

Supporting Information

## Exploring of high-voltage Mg<sup>2+</sup>/Na<sup>+</sup> co-intercalation reaction of Na<sub>3</sub>VCr(PO<sub>4</sub>)<sub>3</sub> in Mg-ion batteries

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**Table S1:** XPS parameters calculated from the deconvolution of V2p spectra of NVCP, NVCP-I<sub>2</sub>, NVCP-Cl<sub>2</sub> and NVCP-NO<sub>2</sub>BF<sub>4</sub>.

Sample	Assignments	B.E. / eV	FWHM / eV	Contrib. / %
NVCP	V <sup>3+</sup> 2p <sub>3/2</sub>	516.5	2.7	30.6
	V <sup>3+</sup> 2p <sub>1/2</sub>	522.6	3.3	53.4
	O1s (sat.)	520.4	1.2	16
NVCP-I <sub>2</sub>	V <sup>3+</sup> 2p <sub>3/2</sub>	516.3	1.9	7.2
	V <sup>4+</sup> 2p <sub>3/2</sub>	517.5	2.0	20.2
	V <sup>3+</sup> 2p <sub>1/2</sub>	522.2	2.1	22.4
	V <sup>4+</sup> 2p <sub>1/2</sub>	524.3	2.3	8.4
	O1s (sat.)	520.3	2.0	41.8
NVCP-Cl <sub>2</sub>	V <sup>3+</sup> 2p <sub>3/2</sub>	516.1	1.6	5.7
	V <sup>4+</sup> 2p <sub>3/2</sub>	517.4	1.5	9.9
	V <sup>5+</sup> 2p <sub>3/2</sub>	518.6	1.4	4.4
	V <sup>3+</sup> 2p <sub>1/2</sub>	522.3	1.7	15.6
	V <sup>4+</sup> 2p <sub>1/2</sub>	523.6	1.7	17.4
	V <sup>5+</sup> 2p <sub>1/2</sub>	525.0	1.7	10.9
	O1s (sat.)	520.6	2.1	36.1
NVCP-NO <sub>2</sub> BF <sub>4</sub>	V <sup>3+</sup> 2p <sub>3/2</sub>	517.2	1.0	2.6
	V <sup>4+</sup> 2p <sub>3/2</sub>	518.4	1.4	16.9
	V <sup>5+</sup> 2p <sub>3/2</sub>	519.3	1.6	1.6
	V <sup>3+</sup> 2p <sub>1/2</sub>	522.3	1.5	13.4
	V <sup>4+</sup> 2p <sub>1/2</sub>	523.5	1.5	17.1
	V <sup>5+</sup> 2p <sub>1/2</sub>	524.8	1.6	4.8
	O1s (sat.)	521.1	1.6	28.5

(B.E. Binding energy; FWHM: Full Width at Half Maximum; Contrib.: Relative contribution in percent).

**Table S2:** XPS parameters calculated from the deconvolution of Cr2p spectra of NVCP, NVCP-I<sub>2</sub>, NVCP-Cl<sub>2</sub> and NVCP-NO<sub>2</sub>BF<sub>4</sub>.

Sample	Assignments	B.E. / eV	FWHM / eV	Contrib. / %
NVCP	Cr <sup>3+</sup> 2p <sub>3/2</sub>	577.8	2.6	52.3
	Cr <sup>3+</sup> 2p <sub>3/2</sub> (sat.)	580.4	4.7	17.0
	Cr <sup>3+</sup> 2p <sub>1/2</sub>	587.4	2.8	26.2
	Cr <sup>3+</sup> 2p <sub>1/2</sub> (sat.)	590.3	2.6	4.5
NVCP-I <sub>2</sub>	Cr <sup>3+</sup> 2p <sub>3/2</sub>	577.5	2.8	63.2
	Cr <sup>3+</sup> 2p <sub>3/2</sub> (sat.)	580.0	3.9	10.4
	Cr <sup>3+</sup> 2p <sub>1/2</sub>	587.1	2.6	23.4
	Cr <sup>3+</sup> 2p <sub>1/2</sub> (sat.)	589.2	1.5	3.0
NVCP-Cl <sub>2</sub>	Cr <sup>3+</sup> 2p <sub>3/2</sub>	577.2	3.3	53.8
	Cr <sup>3+</sup> 2p <sub>3/2</sub> (sat.)	580.2	3.6	12.7
	Cr <sup>3+</sup> 2p <sub>1/2</sub>	586.8	3.9	29.5
	Cr <sup>3+</sup> 2p <sub>1/2</sub> (sat.)	590.0	3.3	4.0
NVCP-NO <sub>2</sub> BF <sub>4</sub>	Cr <sup>3+</sup> 2p <sub>3/2</sub>	577.3	2.6	46.8
	Cr <sup>3+</sup> 2p <sub>3/2</sub> (sat.)	578.8	2.6	25.1
	Cr <sup>3+</sup> 2p <sub>1/2</sub>	587.2	2.6	25.2
	Cr <sup>3+</sup> 2p <sub>1/2</sub> (sat.)	589.4	2.2	2.9

(B.E. Binding energy; FWHM: Full Width at Half Maximum; Contrib.: Relative contribution in percent).

**Table S3.** ICP-AES results of electrode samples.

<i>Theoretical chemical formulae</i>	<i>Information of the electrodes</i>	<i>ICP-AES Na : Mg : V : Cr : P</i>
$\text{Na}_3\text{VCr}(\text{PO}_4)_3$	Original NVCP material	2.96 : 0 : 1.01 : 0.97 : 3
$\text{Na}_{1.5}\text{VCr}(\text{PO}_4)_3$	After first charge in Na cell (1M $\text{NaClO}_4$ in PC)	1.54 : 0 : 0.98 : 0.96 : 3
$\text{Na}_{1.5}\text{Mg}_{0.75}\text{VCr}(\text{PO}_4)_3$	After first discharge in Mg cell* (0.5 M $\text{Mg}(\text{TFSI})_2$ in DME)	1.53 : 0.68 : 0.99 : 0.98 : 3

\*The NVCP electrode was charged in Na cell at  $-15^\circ\text{C}$  to remove the  $\text{Na}^+$  ions. Afterwards, the electrode was washed with DME (1,2-dimethoxyethane) to remove all  $\text{Na}^+$  ions from the electrolyte. Eventually, the electrode is assembled in Mg cell at  $-15^\circ\text{C}$  and discharged to reach 85 mAh/g.

## ICP Results:

## Measurement data for original NVCP material

Quantitative analysis ICP-AES					
Sample ID: NVCP-X DIGESTION 1 (V Cr P Na) 0.0298 1_100					
Blank File: C:\Users\ICP-AES\User\Documents\IRIS\Intrepid\XSP\ThermoElectron\Ortiz\blank047					
Initial Sample Quantity (mg): 29.8					
Sample Prep Volume (mL): 10.00					
Diluted to volume (mL): 100.0					
Aliquot Volume (mL): 1.0					
RESULTS					
Element	Mass	Average Conc.	Unit	Blank Int.	Meas. Intens. Mean
Na	23	68199.601	ppm	283321.468	187400357.228
P	31	94305.172	ppm	20268.705	6149095.136
Rh	103		ppb	991478.513	906465.805
Sample ID: NVCP-X DIGESTION 1 (V Cr P Na) 0.0298 1_1000					
Blank File: C:\Users\ICP-AES\User\Documents\IRIS\Intrepid\XSP\ThermoElectron\Ortiz\blank047					
Initial Sample Quantity (mg): 29.8					
Sample Prep Volume (mL): 10.00					
Diluted to volume (mL): 1000.0					
Aliquot Volume (mL): 1.0					
RESULTS					
Element	Mass	Average Conc.	Unit	Blank Int.	Meas. Intens. Mean
V	51	51637510.214	ppb	3790.678	15519222.777
Cr	52	50564829.721	ppb	4028.103	14146125.162
Rh	103		ppb	991478.513	946977.425

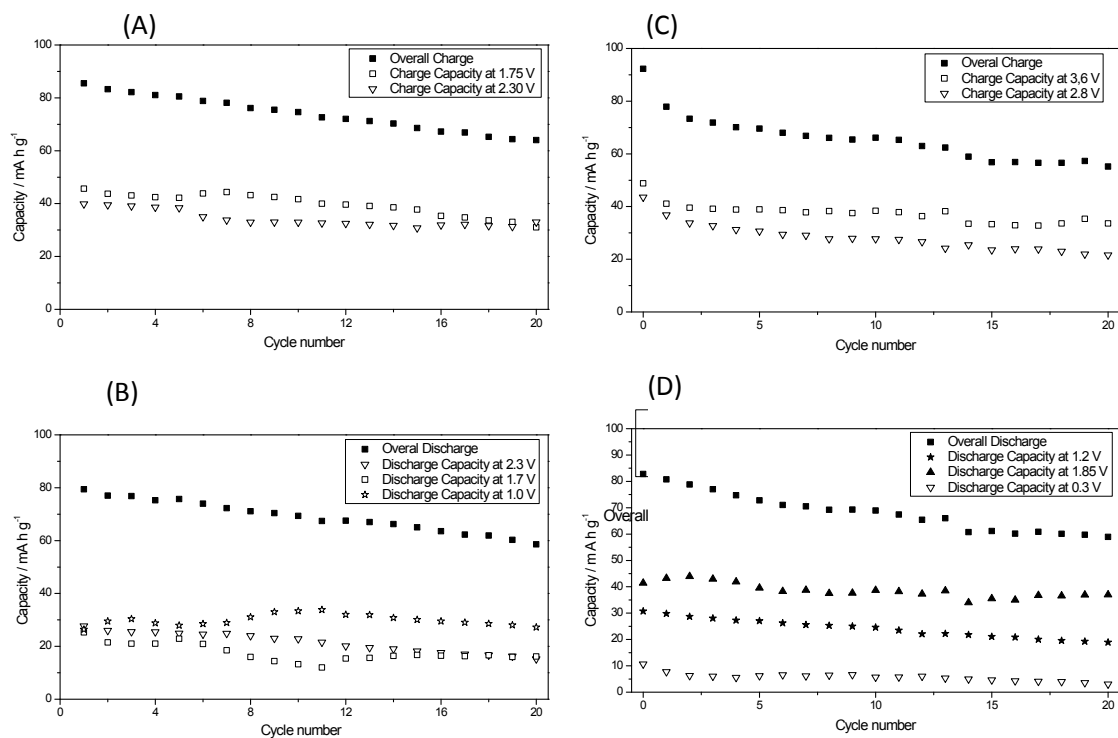
# Supporting Information

## Measurement data of NVCP after first charge in Na cell (1M NaClO<sub>4</sub> in PC)

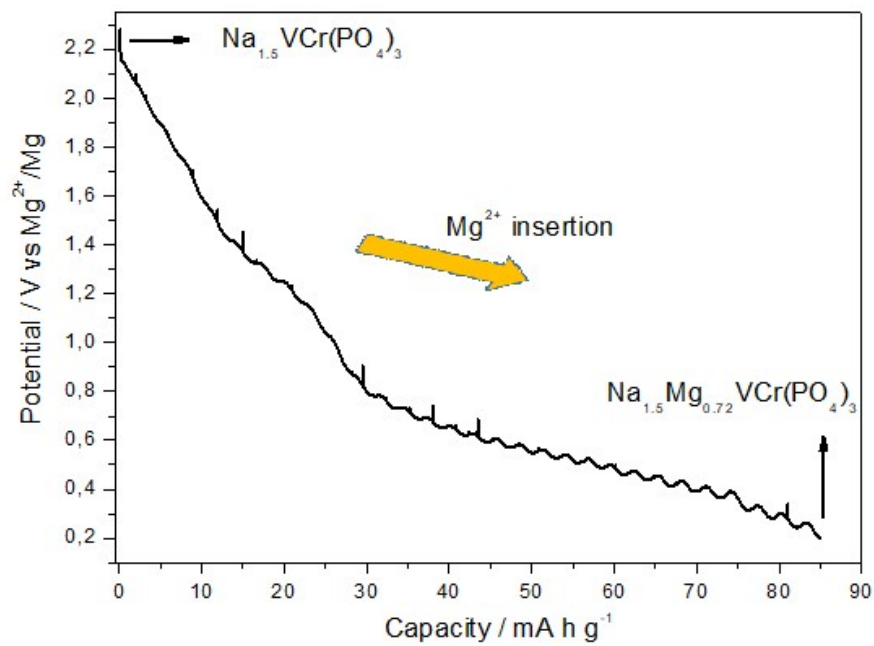
Quantitative analysis ICP-AES					
Sample ID: NVCP-Ch DIGESTION 1 (V Cr P Na) 0.0256 1_100					
Blank File: C:\Users\ICP-AES\User\Documents\IRIS\Intrepid\XSP\ThermoElectron\Ortiz\NVCP-Charged_Na					
Initial Sample Quantity (mg): 25.6					
Sample Prep Volume (mL): 10.00					
Diluted to volume (mL): 100.0					
Aliquot Volume (mL): 1.0					
RESULTS					
Element	Mass	Average Conc.	Unit	Blank Int.	Meas. Intens. Mean
Na	23	35525.821	ppm	301370.468	125404154.207
P	31	95627.533	ppm	19802.215	5148090.230
Rh	103		ppb	987412.012	9210615.015
Sample ID: NVCP-Ch DIGESTION 1 (V Cr P Na) 0.0256 1_1000					
Blank File: C:\Users\ICP-AES\User\Documents\IRIS\Intrepid\XSP\ThermoElectron\Ortiz\NVCP-Charged_Na					
Initial Sample Quantity (mg): 25.6					
Sample Prep Volume (mL): 10.00					
Diluted to volume (mL): 1000.0					
Aliquot Volume (mL): 1.0					
RESULTS					
Element	Mass	Average Conc.	Unit	Blank Int.	Meas. Intens. Mean
V	51	50242140.235	ppb	3641.875	147619222.777
Cr	52	50155090.925	ppb	2468.665	131461895.241
Rh	103		ppb	978048.014	935977.254

## NVCP after first discharge in Mg cell\*

Quantitative analysis ICP-AES					
Sample ID: NVCP-ChNa+DchMg DIGESTION 1 (V Cr P Na) 0.0218 1_100					
Blank File: C:\Users\ICP-AES\User\Documents\IRIS\Intrepid\XSP\ThermoElectron\Ortiz\NVCP-Charged_Na-dchMg					
Initial Sample Quantity (mg): 21.76					
Sample Prep Volume (mL): 10.00					
Diluted to volume (mL): 100.0					
Aliquot Volume (mL): 1.0					
RESULTS					
Element	Mass	Average Conc.	Unit	Blank Int.	Meas. Intens. Mean
Na	23	35292.246	ppm	360214.468	138704694.122
P	31	95627.533	ppm	18920.521	5822020.637
Mg	24	16417.086	ppm	19002.025	3925622.658
Rh	103		ppb	990345.478	9210615.015
Sample ID: NVCP-ChNa+DchMg DIGESTION 1 (V Cr P Na) 0.0218 1_1000					
Blank File: C:\Users\ICP-AES\User\Documents\IRIS\Intrepid\XSP\ThermoElectron\Ortiz\NVCP-Charged_Na-dchMg					
Initial Sample Quantity (mg): 21.76					
Sample Prep Volume (mL): 10.00					
Diluted to volume (mL): 1000.0					
Aliquot Volume (mL): 1.0					
RESULTS					
Element	Mass	Average Conc.	Unit	Blank Int.	Meas. Intens. Mean
V	51	50719546.028	ppb	4241.802	107615602.640
Cr	52	51027638.014	ppb	3408.546	98461715.232
Rh	103		ppb	995048.023	9538531.359



**Figure S1.** Capacity versus cycle number during (a) charge (overall, 1.75 V and 2.3 V region) and (b) discharge (overall, 2.3 V, 1.7V and 1.0 V region) of Mg/NVCP cell recorded at 2 mA g<sup>-1</sup> using 0.5M Mg(TFSI)<sub>2</sub> in DME at - 15°C. Capacity versus cycle number during (c) charge (overall, 2.8 V and 3.6 V region) and (d) discharge (overall, 0.3 V, 1.2V and 1.85 V region) of AC/NVCP cell at - 15°C.



**Figure S2.** Galvanostatic discharge curve of  $\text{Na}_{1.5}\text{VCr}(\text{PO}_4)_3$  electrode material in Mg cell using 0.5 M  $\text{Mg}(\text{TFSI})_2$  in DME using  $2 \text{ mA g}^{-1}$  of current density and recorded at  $-15^\circ\text{C}$ .