Supporting Information

High rate capability $Li_3V_{2-x}Ni_x(PO_4)_3/C$ (x = 0, 0.05, and 0.1) cathodes for Li-ion asymmetric supercapacitors

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a. Chemical and Structural Characterization of LVP/C, LVNP/C2.5, LVNP/C5 cathode materials

Table S1. Carbon content of LVP/C, LVNP/C2.5, LVNP/C5 samples based on TG analysis and LI:V:Ni:P ratio on ICP-OES data.

Samples	Carbon content %	Li	V	Ni	P
LVP/C	4.1	2.99	2.00	-	3.00
LVNP/C2.5	4.2	3.00	1.94	0.04	2.98
LVNP/C5	4.5	2.98	1.88	0.08	2.99

Figure S1. XRD Rietveld refinements of LVP/C a), LVNP/C2.5 b), and LVNP/C5 c). The curves reported in the graph correspond to the observed (black cross) and calculated (red line) pattern obtained after the Rietveld refinement. In the bottom, the difference curve (blue line) and the peak positions (pink bars) are also shown.

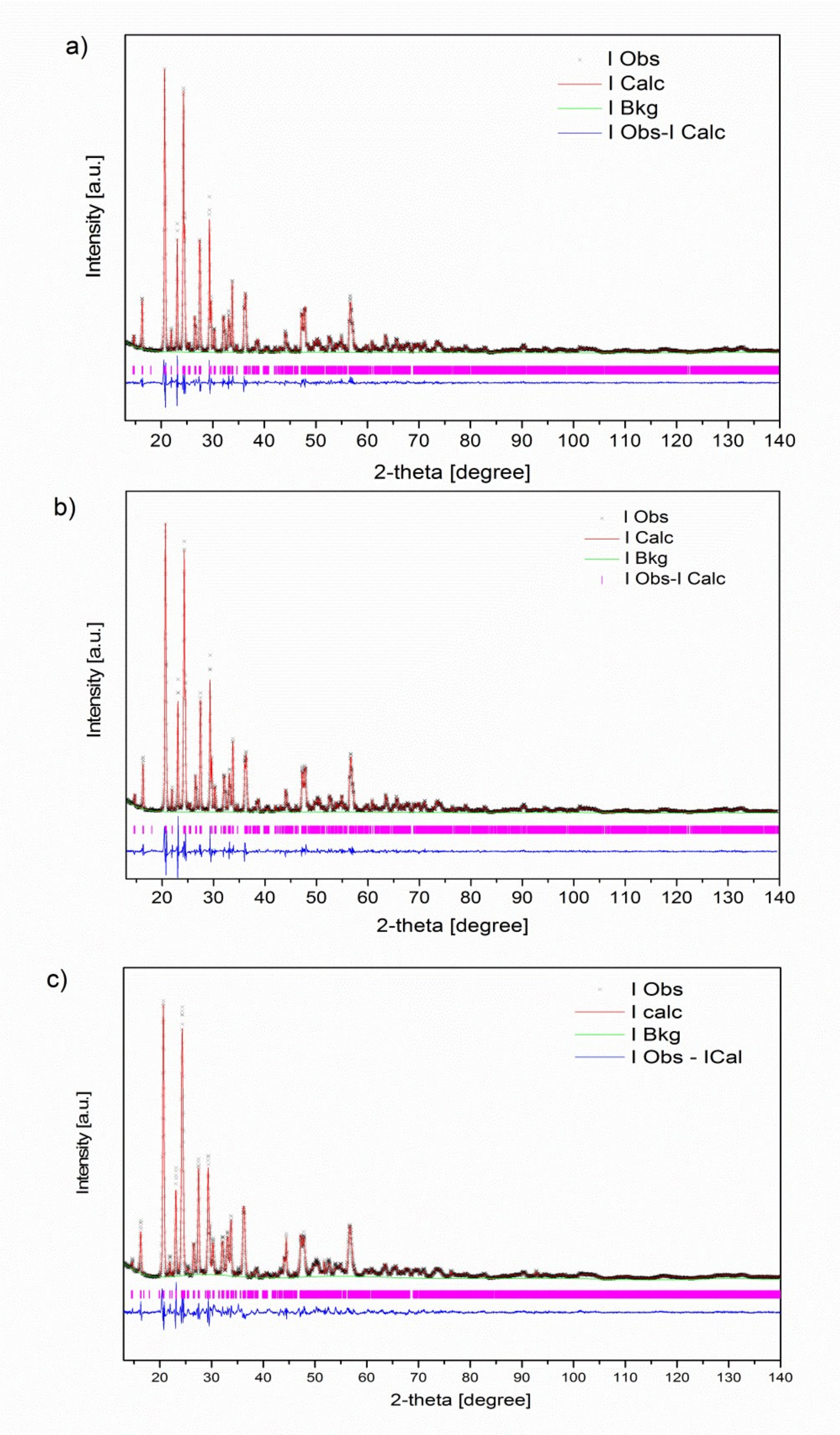

Table S2. Lattice parameters, interatomic distances, disagreement indexes and weight percentage of detected impurities obtained by Rietveld refinement carried out on LVP/C, LVNP/C2.5 and LVNP/C5 samples. The amount of Ni doping in the LVP/C structure has been expressed as Ni/(Ni+V) ratio.

	LVP/C	**LVNP/C2.5**	**LVNP/C5**
Ni/(Ni+V)%	0	2.5	5.0
a (Å)	8.609	8.609	8.600
b (Å)	8.597	8.597	8.597
c (Å)	12.045	12.045	12.041
β	90.58	90.57	90.43
V_0 (Å^3)	891.40	891.54	890.46
Disagreement indexes/%			
R_{wp}	10.40	11.17	10.81
R_p	7.73	8.06	8.29
R_{F2}	4.26	4.44	6.35
R_F	2.38	2.56	3.58
χ^2	3.46	4.20	5.00
Impurities content/wt.%			
Li_3PO_4	-	-	0.5
Ni	-	-	1.5

b. Electrochemical Characterization of LVP/C, LVNP/C2.5, LVNP/C5 electrodes

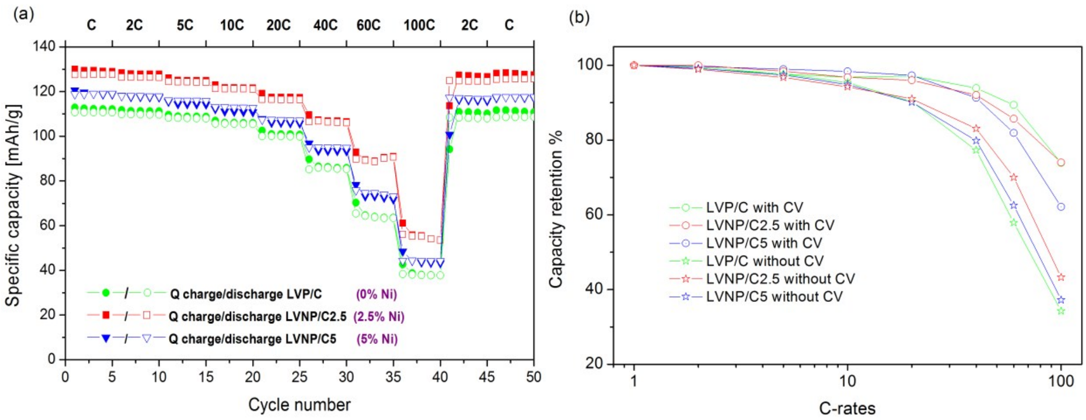

Figure S2. a) C-rates performances of LVP/C, LVNP/C2.5 and LVNP/C5 cathodes, without constant voltage step of 30 seconds in charge, between 3.0-4.3V vs. Li^+/Li, and the corresponding capacity retention b).

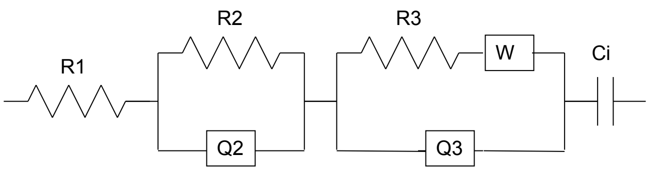

Figure S3. Equivalent circuit used for simulating the experimental impedance data of LVP/C; R1 is the resistance of the electrolyte, R_2 is the resistance and Q_2 capacitance of SEI (and contact). R_3 is the charge transfer resistance and Q_3 the associated capacitance (at medium frequencies), W represents the Warburg diffusion element and Ci the intercalation capacitance.

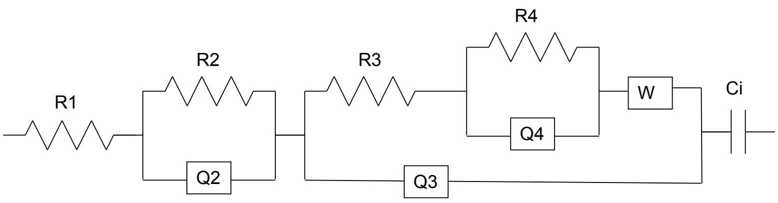

Figure S4. Equivalent circuit used for simulating the experimental impedance data of LVNP/C2.5 and LVNP/C5 electrodes. A further resistance associated with a constant phase element (R_4 and Q_4) has been added in order to fit the arc at low frequencies (interfering with the Warburg diffusion element).

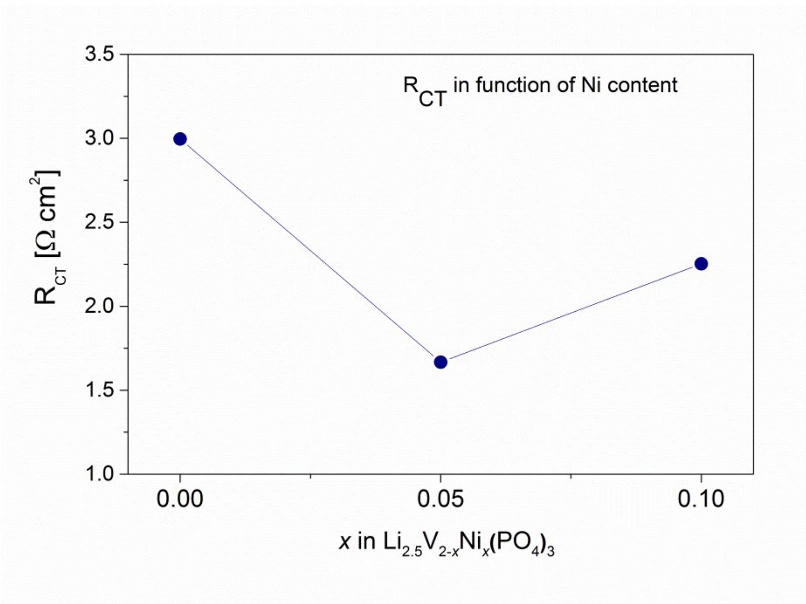

Figure S5. Charge transfer dependence on the basis of Ni content.

c. Cell balancing and Electrochemical Characterization of AC||AC and AC||LVNP/C2.5 systems

The voltage profiles of the symmetric and asymmetric system are displayed in Figure S6. The cell voltage profile of the asymmetric supercapacitor build with LVNP/C2.5 as cathode and AC as anode has been reported in Figure S6b. For sake of comparison also a symmetric AC||AC system has been cycled in the same experimental conditions. The symmetric system shows the typical triangular shape (Figure S6a) with specific capacitances of the cathode and anode of 100 and 90 F g^{-1} (at 0.033 A g^{-1}) in the potential range between 3.0-4.3 V and 3.0-1.6 V vs Li^{+}/Li, respectively. The cell profile of the asymmetric system (Figure S6b) is modified by the presence of the LVNP/C2.5 on the cathode side and all the three plateaus are well defined. During the charge process, the cathode reaches a maximum voltage of 4.3V and the AC anode the minimum voltage of 1.6 V, with a cell voltage of 2.7 V. The dependence of the specific capacity of the two systems with the specific current has been shown in Figure S6c.

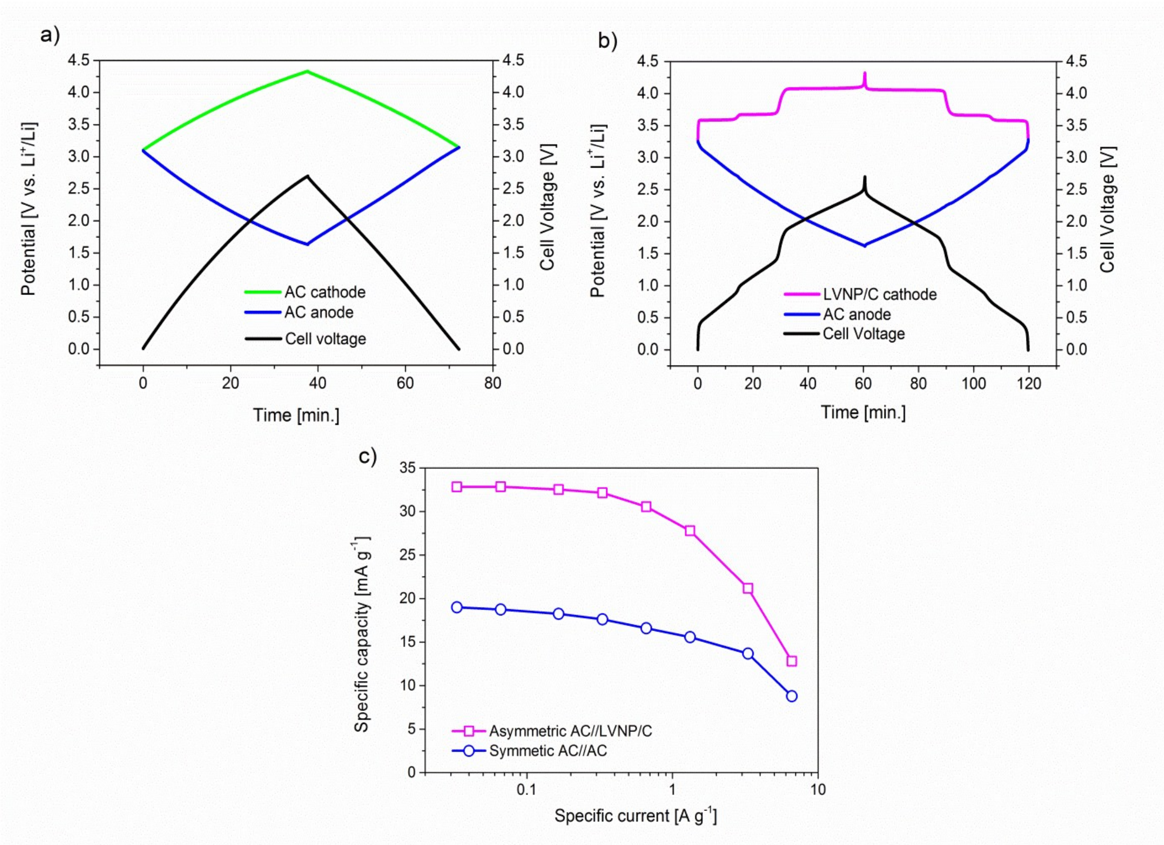

Figure S6. voltage profiles of symmetric a) and asymmetric b) capacitors at the 2nd cycle, in 1M solution of LiPF6 in EC:DMC (1:1); c) rate performance of the symmetric and asymmetric capacitors in the range of specific current between 0.033 and 6.6 A g^{-1}.

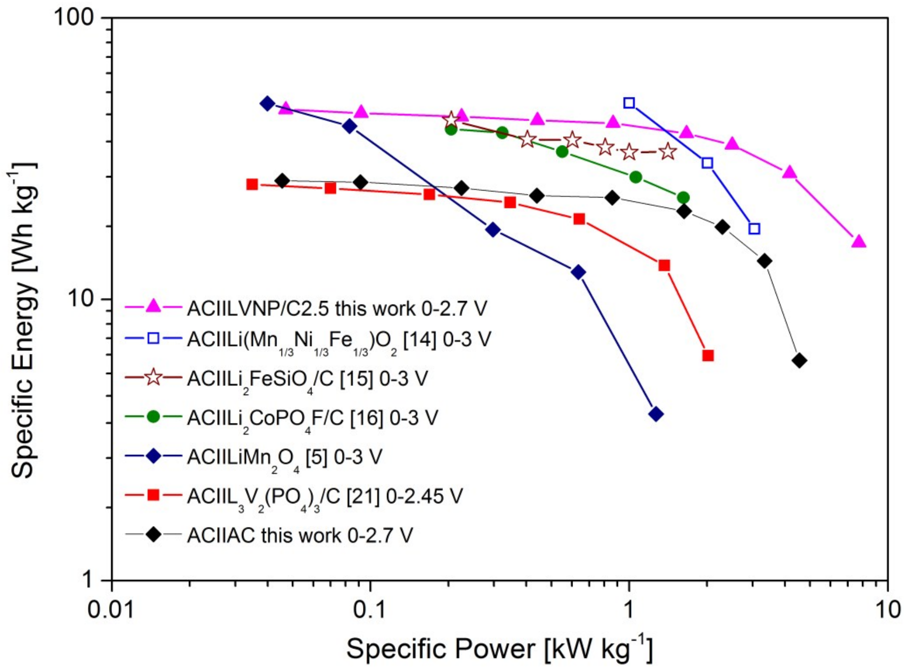

Figure S7. Comparison of the most relevant asymmetric systems in terms of specific power vs. specific energy, with a Li-insertion material as cathode.