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Ligand influence in Li-ion battery hybrid active materials: Ni methylenediphosphonate vs. Ni dimethylamino methylenediphosphonate

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Supplementary information

Methods

Synthesis

NiMeDP and NiDMAMDP were prepared by an adaption of the synthetic procedure described elsewhere.[1] To 20 mL of a 0.15 M tetraethyl methylenediphosphonate (98%, Alfa Aesar) 1 eq. Ni acetate tetrahydrate (98 %, Alfa Aesar) was added under stirring. Subsequently, the mixture was transferred into an autoclave with Teflon inlet, bubbled with Ar for 15 min and heated under autogenous pressure at 160 °C for 7days. The product was collected after centrifugation and repeated washing with H_2O and ethanol.

Structural characterization

Phase identification was performed using X-ray diffraction (XRD) on a PANalytical Empyrean diffractometer using Cu K_α radiation. For the structure determination, XRD on NiMeDP was measured at the MS powder beamline (X04SA) at the Swiss Light Source (SLS) at PSI, Switzerland using a wavelength of 0.7759 Å, in Debye-Scherrer geometry in a 0.5 mm glass capillary. The high resolution XRD pattern of NiMeDP was indexed and atomic positions were determined by direct methods followed by Fourier synthesis in EXPO2014,[2] and further refined by a Rietveld refinement performed in FullProf 3.0.0.[3]

Scanning Electron Microscopy

The scanning electron microscopy (SEM) images were recorded by a Carl Zeiss UltraTM 55 (Germany) apparatus at a 3 kV voltage using the in-lens detector. The powders were sputtered with gold by Ar plasma.

Electrode preparation and electrochemical measurements

Electrodes were prepared by doctor-blading a suspension of 50 wt-% active material, 40 wt-% SuperC65 (Imerys) carbon black conductive additive and 10 wt-% PVdF (Kynar ®) on Cu foil.

Electrochemical measurements were performed in coin-cell type electrochemical cells. The materials were cycled in constant current/constant potential mode (CC/CP), i.e. galvanostatically at 50 mA/g between 0.1 – 3.0 V vs. Li^+/Li followed by a 5 h potentiostatic step after each half cycle. The Li counter electrode served as pseudo-reference. All potentials subsequently reported are indicated vs. Li^+/Li.

The reported specific charge values are corrected as the contribution of the carbon black to the total specific charge was subtracted (170 mAh/g) as described.[4]

Ex situ X-ray absorption spectroscopy (XAS) at the Ni K-edge was measured at the SuperXAS beamline at SLS using a Si(111) channel-cut monochromator[5] in transmission mode. The XAS data were analyzed using the Demeter software package.[6]

1. S. Schmidt, D. Sheptyakov, J.-C. Jumas, M. Medarde, P. Benedek, P. Novák, S. Sallard and C. Villevieille, *Chemistry of Materials*, 2015, **27**, 7889-7895.
2. A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, *Journal of Applied Crystallography*, 2013, **46**, 1231-1235.
3. J. Rodriguez-Carvajal, 1990.
4. S. Schmidt, S. Sallard, D. Sheptyakov, M. Nachtegaal, P. Novák and C. Villevieille, *Journal of Power Sources*, 2017, **342**, 879-885.
5. O. Müller, M. Nachtegaal, J. Just, D. Lützenkirchen-Hecht and R. Frahm, *Journal of Synchrotron Radiation*, 2016, **23**, 260-266.
6. B. Ravel and M. Newville, *Journal of Synchrotron Radiation*, 2005, **12**, 537-541.

Table S1 Details of the Rietveld refinement of NiMeDP.

R-Factors		
R_p	R_{wp}	R_{exp}
11.6%	14.2%	1.18%

Fitted unit cell parameters			
a [Å]	b [Å]	c [Å]	β
9.636(1)	8.083(1)	9.104 (1)	109.128(1) °

Atomic positions and parameters					
	X [Å]	Y [Å]	Z [Å]	B_{iso}	Occupancy
Ni1	0	0.5	0	1.38(4)	0.5
Ni2	0.112(1)	0.142(1)	0.015(1)	1.70(3)	1
P1	0.888(1)	0.200(1)	0.184(1)	1.15(5)	1
O1	0.963(1)	0.079(1)	0.095(1)	0.5(1)	1
O2	0.876(1)	0.374(1)	0.114(1)	1.6(1)	1
O3	0.975(1)	0.197(1)	0.352(1)	0.7(1)	1
C1	0.723(1)	0.136(1)	0.182(1)	0.6(1)	1
P2	0.709(1)	-0.093(1)	0.217(1)	1.82(6)	1
O4	0.833(1)	-0.127(1)	0.363(1)	1.3(1)	1
O5	0.720(1)	-0.198(1)	0.062(1)	2.8(2)	1
O6	0.555(1)	-0.132(1)	0.241(1)	3.3(1)	1
O7	0.742(1)	0.982(1)	0.799(1)	1.8	1
O8	0.551(1)	-0.016(2)	0.472(2)	1.8	0.427(6)

Bond distances Atom1-Atom2					
Atom 1	Atom 2	d_{12} [Å]	Atom 1	Atom 2	d_{12} [Å]
Ni-O bonds			**P-O bonds**		
Ni1	O2	2.09(1)	P1	O1	1.59(1)
Ni1	O3	2.05(1)	P1	O2	1.53(1)
Ni1	O4	1.96(1)	P1	O3	1.48(1)
Ni2	O1(1)	1.96(1)	P2	O4	1.51(1)
Ni2	O1(2)	2.07(1)	P2	O5	1.59(1)
Ni2	O3	2.12(1)	P2	O6	1.60(1)
Ni2	O4	2.14(1)	**P-C bonds**		
Ni2	O5	1.98(1)	P1	C1	1.67(1)
Ni2	O7	2.04(1)	P2	C1	1.89(1)

Bond angles Atom1-Atom2-Atom3							
Atom 1	Atom 2	Atom 3	Angle [°]		Atom 1	Atom 2	Atom 3	Angle [°]
Ligand bond angles					**O-Ni-O bond angles**			
O1	P1	O2	111(1)		O3	Ni1	O3	180(1)
O1	P1	O3	109(1)		O3	Ni1	O4	85(1)
O2	P1	O3	113(1)		O4	Ni1	O3	96(1)
O1	P1	C1	112(1)		O4	Ni1	O4	180(1)
O2	P1	C1	110(1)		O1(1)	Ni2	O1(2)	74(1)
O3	P1	C1	101(1)		O1(1)	Ni2	O3	89(1)
P1	C1	P2	114(1)		O1(1)	Ni2	O4	94(1)
C1	P2	O4	105(1)		O1(1)	Ni2	O5	175(1)
C1	P2	O5	111(1)		O1(1)	Ni2	O7	87(1)
C1	P2	O6	109(1)		O1(2)	Ni2	O3	98(1)
O4	P2	O5	112(1)		O1(2)	Ni2	O4	169(1)
O4	P2	O6	110(1)		O1(2)	Ni2	O5	101(1)
O5	P2	O6	110(1)		O1(2)	Ni2	O7	91(1)
O-Ni-O bond angles					O3	Ni2	O4	79(1)
O2	Ni1	O2	180(1)		O3	Ni2	O5	92(1)
O2	Ni1	O3	91(1)		O3	Ni2	O7	168(1)
O3	Ni1	O2	89(1)		O4	Ni2	O5	90(1)
O2	Ni1	O4	83(1)		O4	Ni2	O7	90(1)
O4	Ni1	O2	97(1)		O5	Ni2	O7	92(1)

Table S2 EXAFS fit results of pristine NiDMAMDP and NiMeDP.

Path	*N*	$S_0^{2,\dagger}$	*R* [Å]	E_0 [eV]	σ^2	*R-value*
Pristine NiDMAMDP						
Ni-O	6.1±0.4	0.789	2.046±0.005	-2.4±0.7	0.0061±0.0007	0.0081
Ni-P	4±3*		3.18±0.05		0.011±0.017*	
Ni-Ni	2.5±1.7*		3.07±0.04		0.007±0.004*	
Pristine NiMeDP						
Ni-O	6.4±0.5	0.789	2.058±0.004	-2.0±0.6	0.006±0.001	0.0039
Ni-P	4±8*		3.22±0.09		0.01±0.04*	
Ni-Ni	2±3*		3.13±0.01		0.006±0.008*	

* The coordination number and mean square displacement values for P and Ni have a high uncertainty because their peaks strongly overlap due to their close R-values.

† Derived from fitting the corresponding Ni metal foil reference

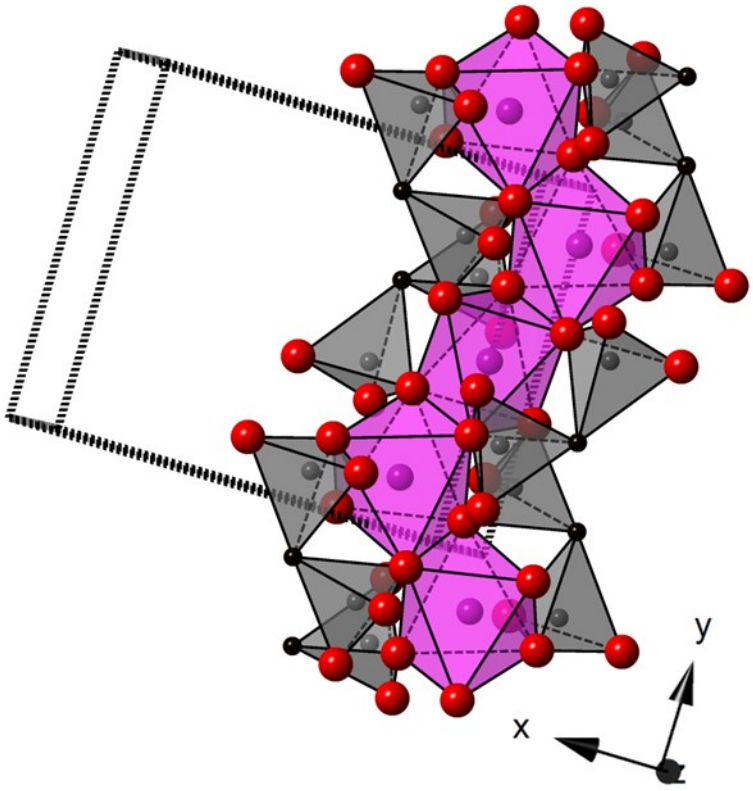

Figure S1 One chain representation of the NiMeDP structure, detail of the Figure 2.B.

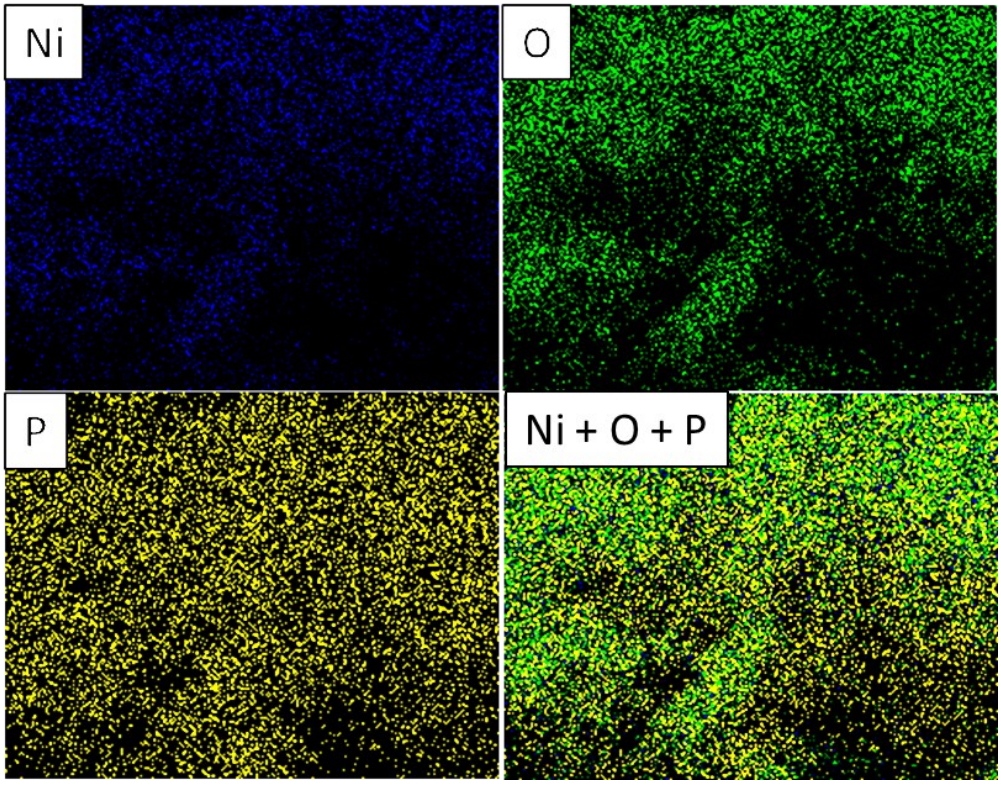

Figure S2 EDX mapping of the pristine NiDMAMDP.

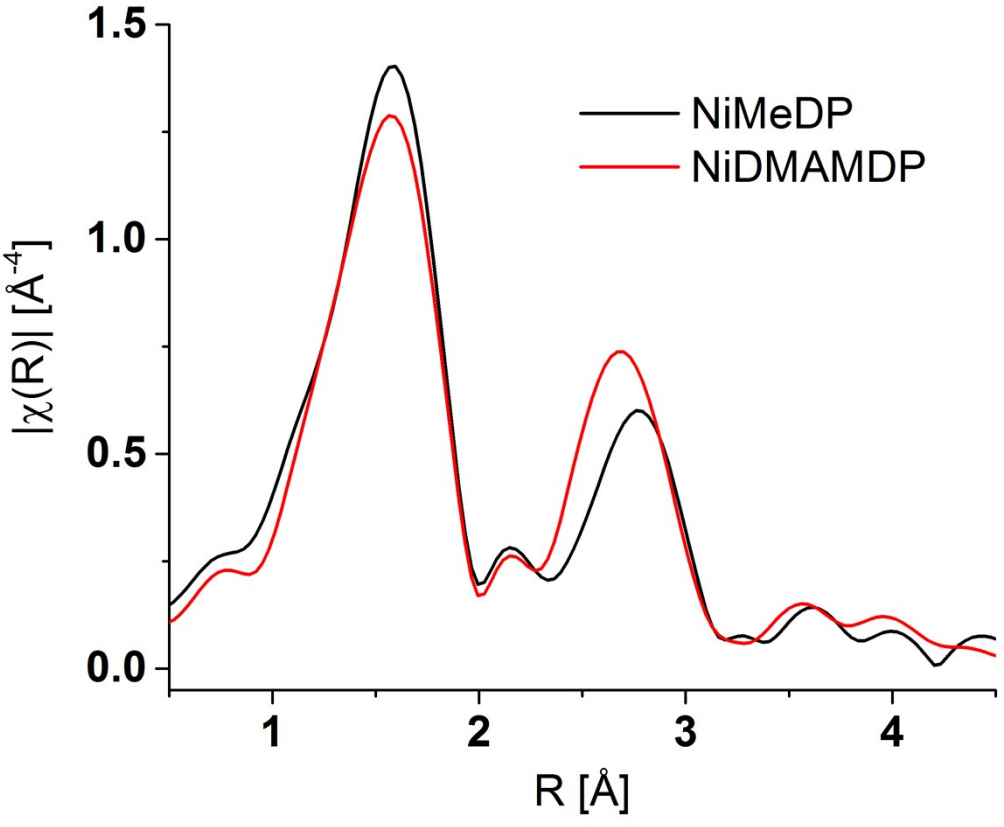

Figure S3 EXAFS spectra in R-space representation of pristine NiMeDP and NiDMAMDP.

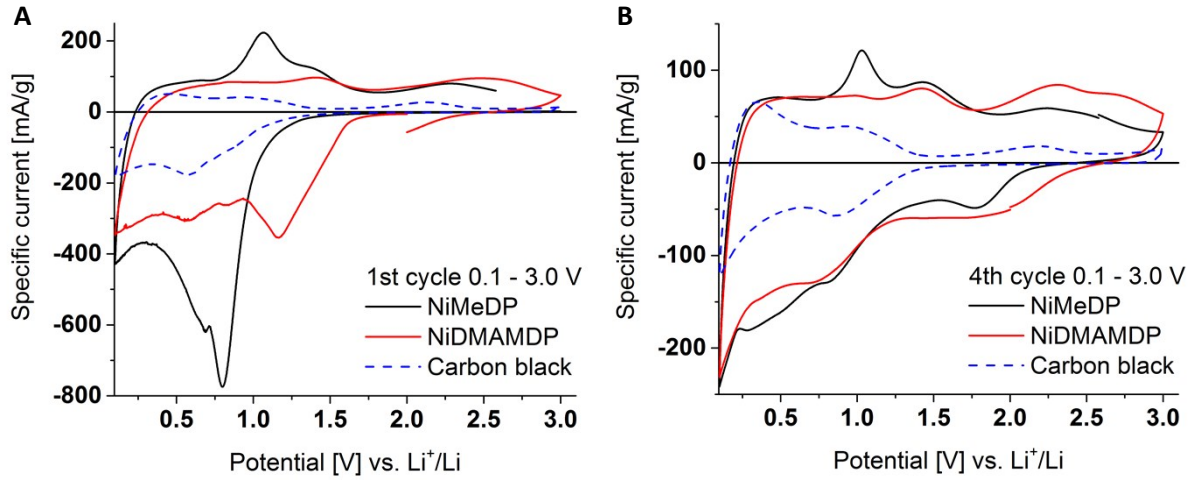

Figure S4 Comparison of the cyclic voltammograms of NiMeDP and NiDMAMDP cycled at 100 μV/s between 0.1 – 3.0 V. **A**: 1st cycle, **B**: 4th cycle.