Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

of

Understanding the electrochemical properties of bulk phase and surface structures of $Na_3T^MPO_4CO_3$ (T^M = Fe, Mn, Co, Ni) from first principles calculations

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Table S1. Calculated E_{FM}-E_{AFM} for $Na_xT^MPO_4CO_3$ compounds

E_{FM}-E_{AFM}	Fe	Mn	Co	E_{FM}-E_{AFM}	Ni
x = 3	0.001	0.001	0.108	x = 3	0.000
x = 2	0.003	-0.002	0.009	x = 2	-0.007
x = 1	0.005	-0.004	0.010	x = 1.5	-0.011
x = 0.5	0.005	-0.026	0.004	x = 1	-0.056
x = 0	-0.011	0.022	0.014	x = 0.5	0.015
				x = 0	-0.036

Table S2. Relaxed parameters and calculated results for surface structures of $Na_3MnPO_4CO_3$ in all orientations

Orientation	Slab (Å)	Relaxation Layer (Å)	Low-energy Termination	Surface Energy (J /m2)	High-energy Termination	Surface Energy (J /m2)
(1 0 0)	27.2	9.0	(0, 0, 0)	1.19	(0.5, 0, 0)	1.60
(0 1 0)	20.5	6.8	(0, 0, 0) and /or (0, 0.5, 0)	0.35	——	——
(0 0 1)	15.7	5.2	(0, 0, 0)	0.44	(0, 0, 0.5)	0.78
(0 1 1)	12.5	4.2	(0, 0, 0)	0.78	(0, 0, 0.5)	0.92
(1 1 0)	16.4	5.5	(0, 0, 0)	0.56	(0.5, 0, 0)	0.68
(1 0 1)	13.7	4.6	(0.5, 0, 0)	0.61	(0, 0, 0)	1.02
(-1 0 1)	13.6	4.5	(0, 0, 0.5)	0.69	(0, 0, 0)	0.96
(1 1 1)	11.4	3.8	(0, 0, 0)	0.51	(0.5, 0, 0)	0.72
(1 2 -1)	13.6	4.6	(0.5, 0, 0)	0.61	(0, 0, 0)	0.86

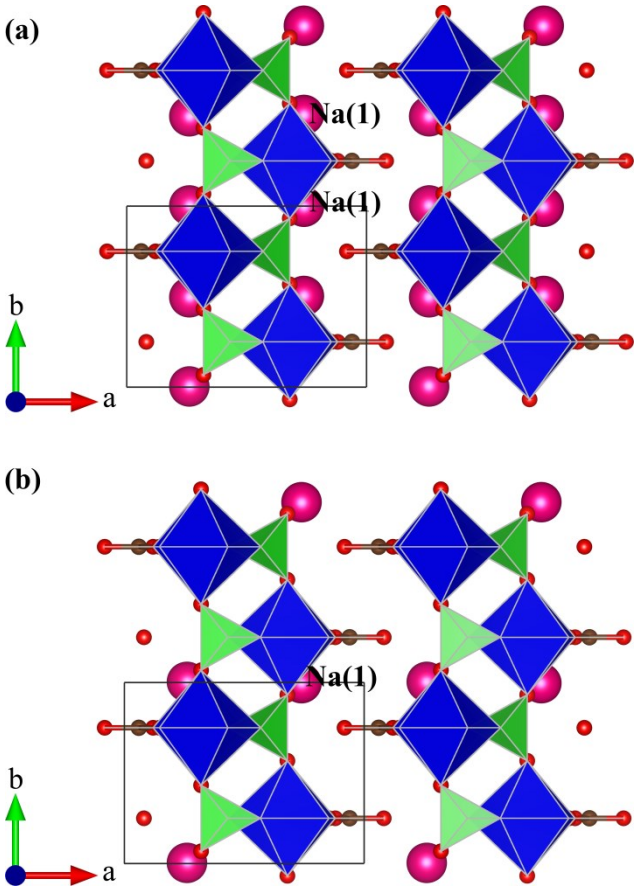

Fig. S1 Calculated crystal structure of (a) $Na_2T^MPO_4CO_3$ and (b) $Na_1T^MPO_4CO_3$ (T^M = Fe, Mn, Co and Ni). (Na atoms, O atoms and C atoms are figured in pink, red and brown, respectively. PO_4 and T^MO_6 are drawn in green and blue, respectively)

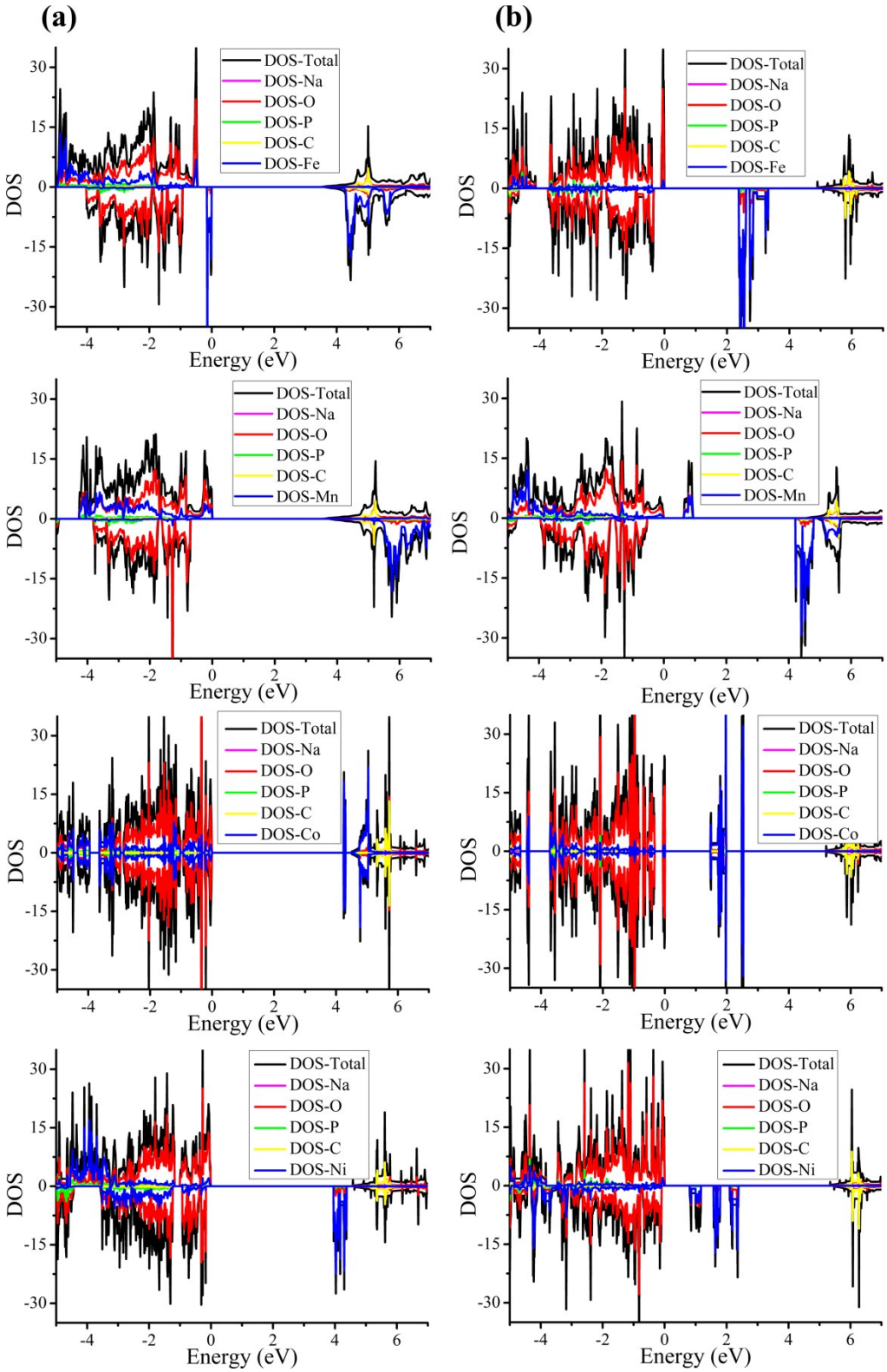

Fig. S2 Calculated local density of states of (a) $Na_3T^MPO_4CO_3$ and (b) $Na_2T^MPO_4CO_3$ (T^M = Fe, Mn, Co, Ni).

Table S3 Calculated average Bader charges for $Na_xT^MPO_4CO_3$ (x = 0, 0.5, 1.0, 1.5, 2, 2.5, 3.0)

x	Na	O	P	C	Fe
0		-1.13	3.76	2.23	1.95
0.5	0.90	-1.20	3.75	2.25	1.95
1	0.90	-1.26	3.74	2.25	1.93
2	0.89	-1.37	3.72	2.20	1.90
3	0.88	-1.42	3.70	2.16	1.45
x	**Na**	**O**	**P**	**C**	**Mn**
0		-1.13	3.75	2.20	1.96
0.5	0.91	-1.19	3.74	2.20	1.94
1	0.91	-1.25	3.73	2.21	1.92
2	0.89	-1.35	3.71	2.22	1.77
3	0.88	-1.43	3.70	2.16	1.52
x	**Na**	**O**	**P**	**C**	**Co**
0		-1.11	3.75	2.24	1.77
0.5	0.90	-1.17	3.74	2.25	1.75
1	0.90	-1.23	3.73	2.25	1.73
2	0.89	-1.34	3.72	2.20	1.71
3	0.88	-1.41	3.70	2.15	1.35
x	**Na**	**O**	**P**	**C**	**Ni**
0		-1.09	3.75	2.24	1.61
0.5	0.90	-1.12	3.75	2.25	1.41
1	0.90	-1.18	3.74	2.25	1.40
1.5	0.89	-1.24	3.72	2.25	1.39
2	0.89	-1.32	3.71	2.25	1.50
3	0.88	-1.40	3.70	2.16	1.32

Standard deviation: Na, P, C: < 0.005; T^M: < 0.02; O: < 0.2

Table S4 Calculated C_{11}, C_{22}, C_{33}, and eigenvalues of the elastic stiffness matrixes for $Na_xT^MPO_4CO_3$

Fe	x=3	x=2	x=1	x=0.5	x=0
Eigenvalue 1	199.3	166.2	97.9	98.4	88.5
Eigenvalue 2	84.2	71.9	47.1	35.3	35.3
Eigenvalue 3	65.4	51.0	33.7	15.6	9.3
Eigenvalue 4	27.5	16.8	16.7	12.2	6.5
Eigenvalue 5	16.1	15.7	4.9	4.1	4.3
Eigenvalue 6	10.6	11.3	4.2	2.2	3.1
C_{11}	135.9	80.5	38.8	13.0	6.9
C_{22}	119.4	140.8	93.6	96.5	88.4
C_{33}	91.5	66.0	41.6	35.2	33.6
Mn	x=3	x=2	x=1	x=0.5	x=0
Eigenvalue 1	183.8	142.5	154.4	161.2	178.8
Eigenvalue 2	73.7	52.3	68.7	57.3	41.8
Eigenvalue 3	58.0	27.3	43.2	22.9	14.5
Eigenvalue 4	26.5	21.6	19.5	16.4	8.7
Eigenvalue 5	23.2	19.2	10.6	12.7	4.5
Eigenvalue 6	7.8	14.9	7.5	6.6	1.7
C_{11}	129.5	78.4	57.8	34.4	4.5
C_{22}	101.4	72.2	142.0	160.6	178.8
C_{33}	82.4	68.8	60.0	45.1	40.7
Co	x=3	x=2	x=1	x=0.5	x=0
Eigenvalue 1	197.9	183.1	97.7	111.4	93.0
Eigenvalue 2	77.1	73.8	49.7	29.0	39.8
Eigenvalue 3	63.5	60.4	38.1	17.8	15.6
Eigenvalue 4	32.5	18.6	11.1	11.9	11.9
Eigenvalue 5	26.3	14.4	3.7	6.8	6.3
Eigenvalue 6	10.0	12.3	1.6	2.7	5.9
C_{11}	133.3	90.2	43.0	19.1	21.1
C_{22}	103.2	151.3	92.4	110.0	92.1
C_{33}	99.4	74.5	42.7	25.2	35.1

Ni	x=3	x=2	x=1.5	x=1	x=0.5	x=0
Eigenvalue 1	207.1	165.5	109.3	92.0	76.5	114.5
Eigenvalue 2	81.3	72.7	56.3	54.6	27.8	39.6

Eigenvalue 3	72.4	58.5	45.9	22.6	12.8	15.8
Eigenvalue 4	35.8	24.7	20.6	10.2	10.7	8.5
Eigenvalue 5	28.4	16.6	13.4	6.4	4.2	7.6
Eigenvalue 6	12.1	13.9	10.5	5.8	2.9	5.9
C_{11}	142.7	91.2	60.6	37.9	11.9	18.2
C_{22}	109.8	127.4	84.5	87.1	72.8	113.9
C_{33}	106.7	77.9	65.0	43.0	29.8	37.5

Table S5 Coordination number of Mn and Na ions located in the outmost layers of the surfaces

Surface	Label	Coordination number[a]	Surface	Label	Coordination number[a]
100	Na(1)	2-2	101	Na(1)	3-4
	Na(2)	5-5		Na(2)	3-4
	Na(3)	5-5		Na(3)	4-4
	Mn(1)	6-6		Mn(1)	5-5
010	Na(1)	3-3	-101	Na(1)	2-4
	Mn(1)	5-5		Na(2)	5-5
001	Na(1)	4-5		Na(3)	5-5
	Na(2)	4-5		Na(4)	5-6
	Na(3)	4-4		Na(5)	5-6
	Mn(1)	5-5		Mn(1)	3-4
110	Na(1)	6-6	111	Na(1)	4-4
	Na(2)	5-5		Na(2)	3-4
	Na(3)	4-5		Na(3)	5-5
	Mn(1)	3-5		Na(4)	5-5
011	Na(1)	4-4		Mn(1)	4-4
	Na(2)	5-5	12-1	Na(1)	3-3
	Na(3)	5-5		Na(2)	4-4
	Mn(1)	5-5		Na(3)	4-4
	Mn(3)	5-5		Mn(1)	5-5
				Mn(2)	4-4

[a] Coordination of atoms in unrelaxed surface structures - Coordination of atoms in relaxed surface structures