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Supplementary Information

Ion Diffusion Mechanism in *Pn* $Na_xLi_{2-x}MnSiO_4$

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We have performed the bader analysis[S1-S3] of the charge population around A1 and A2 sites (see Fig.1) in $Na_xLi_{2-x}MnSiO_4$ (x = 2, 1, 0), as shown in Table S1. It is shown that compared with that in Li_2MnSiO_4, there are a little more charge accumulated around the A1 (or A2) site in Na_2MnSiO_4, indicating more covalent Na-O bonds than Li-O bonds. However, the atomic volume around the A1 (A2) site in Na_2MnSiO_4 is significantly larger (~ three times) than that in Li_2MnSiO_4, which is consistent with our bond length analysis and conclusions that Na_2MnSiO_4 can supply wider ionic diffusion channels than Li_2MnSiO_4.

Table S1. Calculated bader charge and atomic volume

	Li_2MnSiO_4		Na_2MnSiO_4		$NaLiMnSiO_4$	
	A1	A2	A1	A2	A1	A2
Charge	0.138	0.146	0.186	0.196	0.139	0.194
Atomic Volume	3.364	3.215	9.275	8.904	3.359	8.660

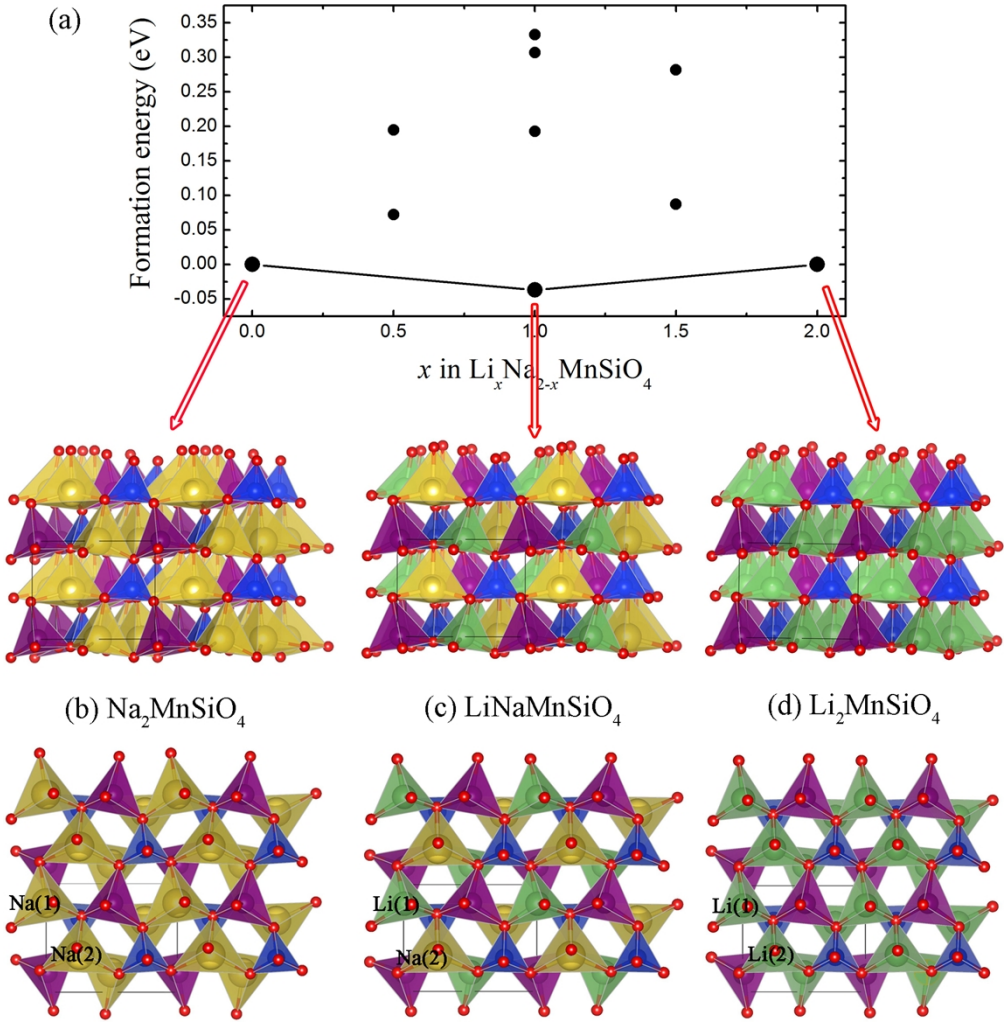

Fig. S1 (a) Calculated formation energies of $Li_xNa_{2-x}MnSiO_4$ ($0<x<2$) structures. The stable configurations are given in (b) Na_2MnSiO_4 (c) $LiNaMnSiO_4$ and (d) Li_2MnSiO_4.

The calculated formation energies of several $Li_xNa_{2-x}MnSiO_4$ structures with different x values within one unit cell are shown in Fig. S1. It is shown that for $NaLiMnSiO_4$, only the structural with Li^+ and Na^+ ions respectively occupying the A1 and A2 sites is stable, with respect to the decomposition to Li_2MnSiO_4 and Na_2MnSiO_4. Moreover, this stable configuration can well reproduce the experimental results reported by Duncan et al (ref. 16 in main paper). Thus the further calculations in this work are based on it.

References

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S2. E. Sanville, S. D. Kenny, R. Smith and G. Henkelman, *J. Comput. Chem.*, 2007, **28**, 899-908.

S3. W. Tang, E. Sanville and G. Henkelman, *J. Phys.: Condens. Matter*, 2009, **21**, 084204.