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

Supporting Information For

Anomalously high Na^+ and low Li^+ mobility in intercalated $Na_2Ti_6O_{13}$

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Electronic structure of $A_1Na_2Ti_6O_{13}$

In a previous calculation, it was claimed that the electronic structure contributes to the different barriers for Li-diffusion between different interstitial sites in $Na_2Ti_6O_{13}$. In order to examine whether the electronic structure of $Na_1Na_2Ti_6O_{13}$ differs with $Li_1Na_2Ti_6O_{13}$, the GGA+U calculated electronic densities of states (pDOS) are plotted in Figure S1. For the pristine $Na_2Ti_6O_{13}$ the main O 2p based valence band is spread between 0 and -5.1 eV, with respect to the highest occupied state. Ti makes only a small contribution to the valence density of states and hybridizes with O-2p. The conduction band, on the other hand, is mainly composed of Ti-3d, with hybridization with O-2p. Na-3s state is located far above the conduction band and thus does not contribute to the state near Fermi level.

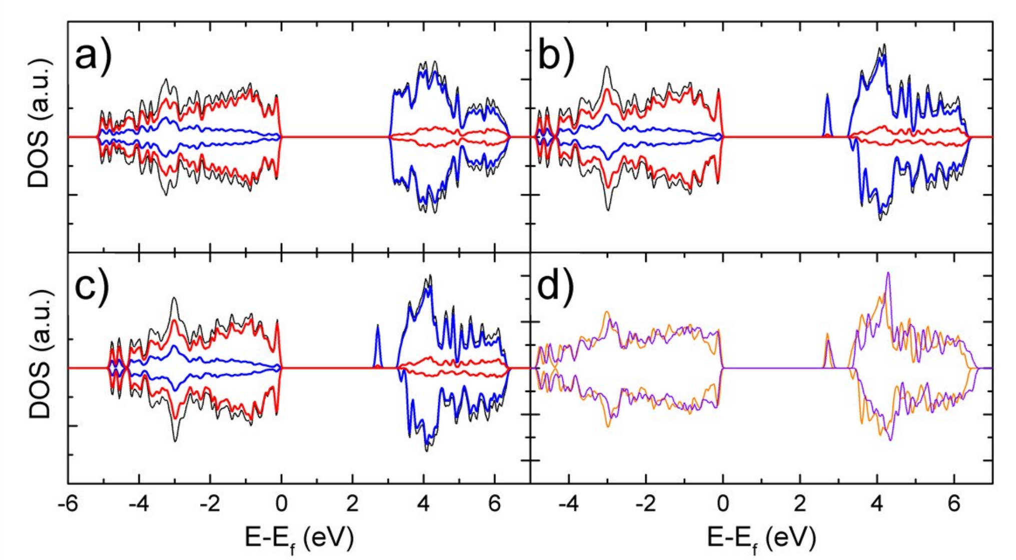

Figure S1. Density of states (DOSs) for (a) $Na_2Ti_6O_{13}$, (b) $Na_1Na_2Ti_6O_{13}$ and (c) $Li_1Na_2Ti_6O_{13}$. In (d), the density of states for $Li_1Na_2Ti_6O_{13}$ with Li at A1 and A2 sites are compared. Red: DOS projected on oxygen; blue: DOS projected on Ti; black: total DOS.

Table S1. Band gap (E_g) and donor states for $Na_2Ti_6O_{13}$, $Na_1Na_2Ti_6O_{13}$ and $Li_1Na_2Ti_6O_{13}$.

		$Na_2Ti_6O_{13}$	$Na_1Na_2Ti_6O_{13}$	$Li_1Na_2Ti_6O_{13}$
E_g (eV)	GGA+U	3.17	3.41	3.48
	GGA	2.2		
	HSE	4.7		
	experimental	3.44 (exp.)		
donor state (eV)			2.72	2.73

When the guest Li^+ or Na^+ ions are inserted, the framework of $(Ti_6O_{13})^{2-}$ is reduced. The projected wave functions at the valance band and conduction band (Fig. S2) show the localization of extra charge at Ti ions that bridge rectangular channels. The reduced Ti state is moved to lower energy level, forming donor state below the conduction band, as shown in Figure S1b-c. Varying the inserted ion only slightly affects the band gaps and the position of the donor states, as listed in Table S1. Furthermore, the position of the guest ion only has negligible effect on the electronic structure. For example, Figure S1d compares the electronic structures for $Li_1Na_2Ti_6O_{13}$ with the guest Li^+ occupying either A1 or A2 sites. The characteristics at band edges and the positions of the donor state are nearly identical. We conclude that the variation of the electronic structure plays a minor role in affecting the diffusion behavior of Li^+ and Na^+ in $Na_2Ti_6O_{13}$.

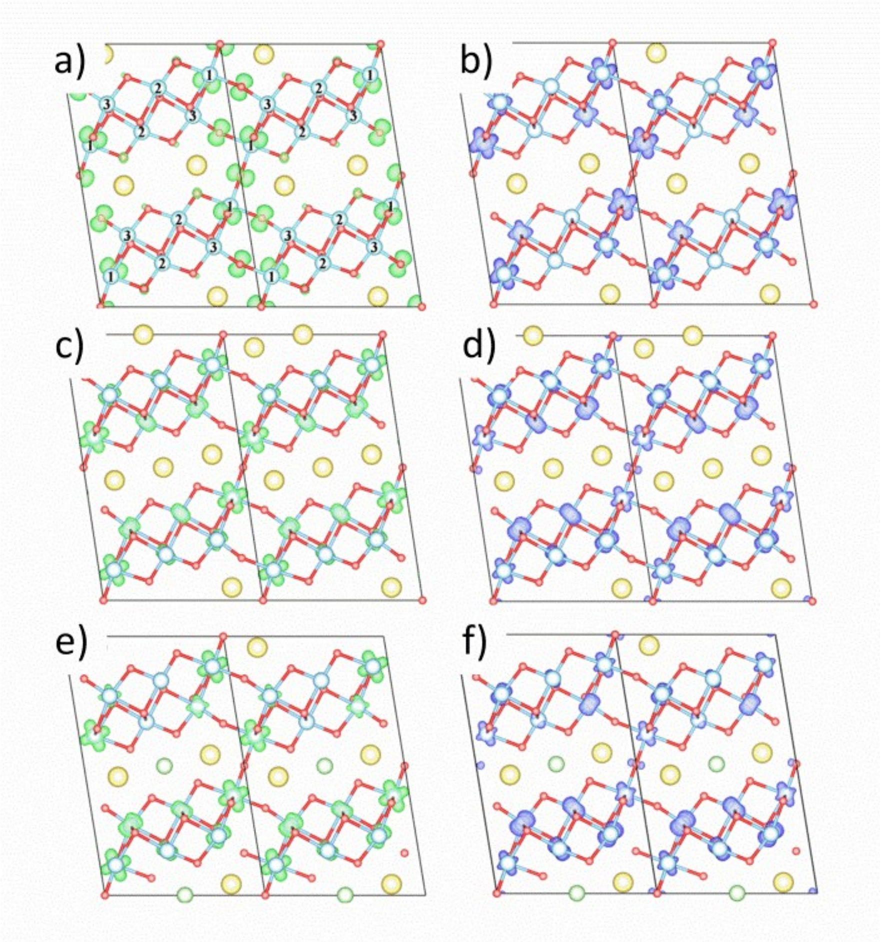

Fig. S2. Projected wave functions at the (a, c, e) conduction band and (b, d, f) conduction band for (a, b) $Na_2Ti_6O_{13}$, (c, d) $Na_1Na_2Ti_6O_{13}$ and (e, f) $Li_1Na_2Ti_6O_{13}$.

Fit the PES using Buckingham potential

We use the form of Buckingham potential to fit the potential energy surface between A1 and A2 site. The Buckingham potential has the form

$$U = A\exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}$$

In our fitting, we neglect the r^6 term and the fitted parameter is shown in Table S3. We should note that the fitting is only for the purpose to understand the PES in $Na_2Ti_6O_{13}$. Thus it should not be directly applied to study other compounds.

Table S2. Fitted parameters in the form of Buckingham potential for Figure 3c.

	A (eV)	ρ (Å)
Na-O	-12.7060	1.8172
Na-Na	0.3680	2.7898
Li-O	-18.176	1.3043
Li-Na	11.0452	0.5542

GGA and GGA+U calculated PES

We examine the dependence of PES on the choice of simulation method by by calculating the relative PES for Na intercalation with GGA and GGA+U. The result is shown in Fig. S3. GGA-PES only differs with GGA+U-PES by less than 0.05 eV for Na intercalation in the frozen lattice. This is consistent with the observation in Table 2 that GGA and GGA+U do not change significantly the diffusion barrier in this special system. Based on these, we believe that the fitting result in Fig. 3c does not depend on the calculation method and we are not attempting to re-calculate using more expensive HSE method.

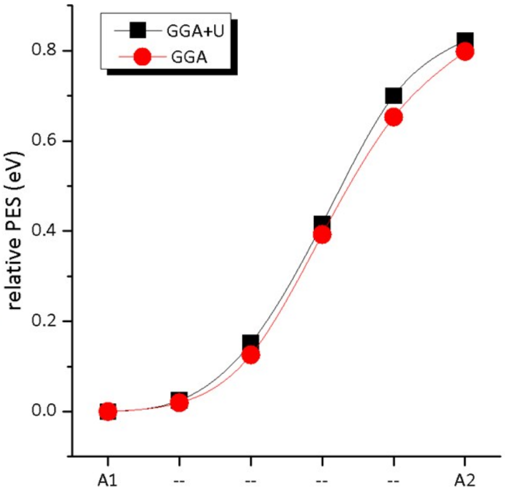

Fig. S3. Potential energy surface (PES) for intercalated Na along A1-A2 path in the frozen lattice of $Na_2Ti_6O_{13}$.